THE GAMMA RADIOLYSIS OF CARBON TETRACHLORIDE AND AMMONIA SOLUTIONS

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SECTION I

INTRODUCTION

Studies in the radiolysis of dilute solutions of carbon tetrachloride generally have been undertaken for one of two reasons: first, to learn more about the radiation chemistry of pure carbon tetrachloride, e.g. radical scavenger studies; and second, to use the irradiated carbon tetrachloride as a source of chlorine atoms and trichloromethyl radicals for either kinetic or synthetic studies.

The present investigation on the radiolysis of carbon tetrachloride and ammonia solutions is mainly concerned with the second of these two objectives.

Review of Earlier Work on the Radiolysis of Carbon Tetrachloride Solutions

A survey of the literature in radiation chemistry has revealed no evidence of earlier studies on the radiolysis of carbon tetrachloride and ammonia solutions. However, several papers have appeared on other carbon tetrachloride systems. For comparison purposes some of these papers will now be reviewed.

One of the earliest studies on the gamma-radiolysis of dilute solutions of carbon tetrachloride was that of Cooper and Stafford.[1] They studied solutions of propane, toluene, benzene, hexadecane, n-decane, and n-dodecane, respectively, in carbon tetrachloride. They found that under gamma-radiolysis paraffinic hydrocarbon solutions lead mainly to the production of hydrogen chloride, alkylchlorides, mixed and straight dimer products plus smaller amounts of chloroform. In the presence of aromatic solutes the predominant reaction of chlorine atoms was still found to be hydrogen abstraction but evidence of direct addition to the aromatic ring was also observed. Radiolysis products included hydrogen chloride, aromatic chlorides, mixed and straight dimers, and smaller quantities of high boiling material not identified.

In the investigations on solutions containing n-decane, hexadecane and n-dodecane, Cooper and Stafford showed that the yield of hydrogen chloride was constant ($G(HCl) = 3.9$) when hydrocarbon concentrations were greater than .04 mole per cent. These results indicate that carbon tetrachloride solutions containing 1% solute should be sufficiently concentrated to eliminate complications due to side reactions from small amounts of impurities.

Heiba and Anderson[2] studied gamma-ray initiated reactions in solutions of carbon tetrachloride and aldehydes. In dilute carbon tetrachloride solutions, the major products formed were the acid chloride, chloroform, and hydrogen chloride. Hexachloroethane was also isolated but was of lesser importance. To explain this product distribution, these authors proposed a chain mechanism involving CCl_3 and $RC = O$ radicals, e.g.

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \qquad (1)$$

$$Cl\cdot + R\overset{H}{C}{=}O \rightarrow R\dot{C}{=}O + HCl \qquad (2)$$

$$CCl_3\cdot + R\overset{H}{C}{=}O \rightarrow R\dot{C}{=}O + HCCl_3 \qquad (3)$$

$$R\dot{C}{=}O + ClCCl_3 \rightarrow RCOCl + CCl_3\cdot \qquad (4)$$

$$CCl_3\cdot + CCl_3\cdot \rightarrow C_2Cl_6 \qquad (5)$$

Spurný[3] has examined oxygen saturated solutions of carbon tetrachloride (1.5×10^{-2}M in oxygen). With X-rays he found $G(Cl_2) = G(COCl_2) = 2.2$ and for cobalt-60 gamma rays $G(Cl_2) = G(COCl_2) = 4.3$. The author was careful to point out that this apparent energy dependence could also involve a dose-rate effect.

Spurný was not able to detect the presence of any chlorine oxides, peroxides, or carbon dioxide as stable products, but thought this reasonable in view of his observation that $G(COCl_2) = 2G(-O_2)$. This author did suggest, however, that both the peroxy radical CCl_3O_2 and chlorine monoxide were important intermediates in the radiolysis of solutions of oxygen and carbon tetrachloride. These species are shown below in reactions (2), (3) and (4):

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \qquad (1)$$

$$CCl_3 + O_2 \rightarrow CCl_3O_2 \qquad (2)$$

$$CCl_3O_2 \rightarrow COCl_2 + ClO \qquad (3)$$

$$ClO + CCl_4 \rightarrow COCl_2 + Cl_2 + Cl\cdot \qquad (4)$$

$$2Cl\cdot \rightarrow Cl_2 \qquad (5)$$

The above mechanism shows that for each molecule of carbon tetrachloride decomposed by ionizing radiation one molecule of phosgene is formed. Thus, the G value for carbon-chlorine bond rupture* is given directly by $G(COCl_2)$ or 4.2. From Cooper's and Stafford's work on hydrocarbon solutions we also have $G(C\text{-}Cl) = G(HCl) = 3.9$.

Chen, Wong, and Johnston[4] studied the gamma radiolysis of chloroform-carbon tetrachloride solutions. Their results indicated that a mole fraction of chloroform as small as .008 could completely inhibit chlorine production. With solutions containing 2 mole per cent chloroform, G(HCl) was found to be 5.00. This would give a somewhat higher value of G(C-Cl) than those estimated from the work of Spurný, and Cooper and Stafford.

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*$G(C\text{-}Cl)$ is defined as the number of carbon-chlorine bonds broken in primary processes per one hundred electron volts of energy absorbed by the system.

More recently Urban and Bednář,[5] and Henglein, Heckel, Ojima, and Meisner[6] have investigated the γ-radiolysis of the system carbon tetrachloride-cyclohexane. Urban and Bednář limited their product analysis to hydrogen chloride. They found that over a cyclohexane concentration range of .8 to 4.5 mole per cent the G value for hydrogen chloride formation was constant at 5.29.

Henglein and coworkers carried out complete product analyses over a wide range of cyclohexane concentrations. For solutions of carbon tetrachloride containing approximately 2 mole per cent cyclohexane, they reported the major radiolysis products and yields as follows: hydrogen chloride, 7.5; hexachloroethane, 5.0; chloroform, 3.5; and cyclohexylchloride, 5.0. The only minor product in this system was trichloromethylcyclohexane. Its G value was about .2. To explain the above results these authors proposed a chain mechanism involving cyclohexyl and trichloromethyl radicals, e.g.

$$CCl_4 \rightarrow CCl_3\cdot + Cl\cdot \quad (1)$$

$$Cl\cdot + c\text{-}C_6H_{12} \rightarrow HCl + c\text{-}C_6H_{11}\cdot \quad (2)$$

$$c\text{-}C_6H_{11}\cdot + CCl_4 \rightarrow c\text{-}C_6H_{11}Cl + CCl_3\cdot \quad (3)$$

$$CCl_3\cdot + c\text{-}C_6H_{12} \rightarrow CCl_3H + c\text{-}C_6H_{11}\cdot \quad (4)$$

$$CCl_3\cdot + c\text{-}C_6H_{11}\cdot \rightarrow c\text{-}C_6H_{11}CCl_3 \quad (5)$$

$$CCl_3\cdot + CCl_3\cdot \rightarrow C_2Cl_6 \quad (6)$$

The reportedly large G value for hydrogen chloride formation in these experiments now appears to be related to the purity of the carbon tetrachloride used. Urgan and Bednár, for example, investigated the effects of the aging of carbon tetrachloride. They found that G(HCl) for freshly purified carbon tetrachloride was approximately 5, however, at the end of 16 weeks this value had increased to 14.

Wiley, Patterson, Chesnut, and Grunhut,[7] in another recent study, examined the gamma-ray induced decomposition of amides in carbon tetrachloride. In this study ten amides, including formamides, acetamides, and anilides were irradiated as 5 mole per cent solutions in carbon tetrachloride. Hydrogen chloride, chloroform, tetrachloroethylene, and hexachloroethane were the major products identified in each of the amide systems. The G values for these compounds are summarized in Table I.

The authors have attempted to explain their data in terms of the following mechanism:

$$\mathrm{CCl_4} \rightsquigarrow \mathrm{Cl\cdot} + \mathrm{CCl_3\cdot} \tag{1}$$

$$\mathrm{RCONR'CH_3} \rightarrow \mathrm{RCONR'CH_2\cdot} + \mathrm{H\cdot} \tag{2}$$

$$\mathrm{CCl_3\cdot} + \mathrm{RCONR'CH_3} \rightarrow \mathrm{CHCl_3} + \mathrm{RCONR'CH_2\cdot} \tag{3}$$

$$\mathrm{RCONR'CH_2\cdot} + \mathrm{CCl_4} \rightarrow \mathrm{RCONR'CH_2Cl} + \mathrm{CCl_3\cdot} \tag{4}$$

$$\mathrm{Cl\cdot} + \mathrm{RCONR'CH_3} \rightarrow \mathrm{HCl} + \mathrm{RCONR'CH_2\cdot} \tag{5}$$

$$\mathrm{H\cdot} + \mathrm{CCl_4} \rightarrow \mathrm{HCl} + \mathrm{CCl_3\cdot} \tag{6}$$

$$\mathrm{RCONR'CH_2Cl} + \mathrm{R'R''NCOR} \rightarrow \mathrm{(RCONR'CH_2NR'R''COR)^+Cl^-} \tag{7}$$

$$\mathrm{2CCl_3\cdot} \rightarrow \mathrm{C_2Cl_6} \tag{8}$$

$$\mathrm{RCONR'CH_3} + \mathrm{HCl} \rightarrow \mathrm{(RCONR'CH_3)HCl} \tag{9}$$

The route by which tetrachloroethylene is formed was not made clear by these workers.

TABLE I

IRRADIATION OF 5 MOLE % AMIDE SOLUTIONS IN CARBON TETRACHLORIDE[a]

Amide	$G(HCl)^b$	$G(CHCl_3)^b$	$G(C_2Cl_6)^b$
$HCONH_2$	10.70	0.24	3.14
$HCONHCH_3$	13.25	0.44	3.14
$HCON(CH_3)_2$	20.94	1.23	3.78
$CH_3CONHCH_3$	11.93	0.47	3.02
$CH_3CON(CH_3)_2$	23.29	1.09	2.85
$HCONHC_6H_5$	13.14	0.25	2.96
$HCON(CH_3)C_6H_5$	15.25	0.67	3.07
$CH_3CON(CH_3)C_6H_5$	16.46	0.41	2.32
$CH_3CON(C_6H_5)_2$	10.03	0.24	1.35
$HCON(C_6H_5)_2$	8.46	0.50	1.67

[a] Dose rate 1.54 to 1.41 x 10^5 rads/hr.; 120 to 130 hours.

[b] Average value for two determinations; reproducibility ± 4.4%.

A value for G(C-Cl) is not available from this work due to the lack of a complete material balance.

Review of Present Study

The present investigation on the gamma-radiolysis of carbon tetrachloride-ammonia solutions represents an extension of the work started by Mr. James Buchanan in 1961, and for which he received his Masters Degree in February of 1962. Results available at that time included the identification of hexachloroethane and ammonium chloride as major radiolysis products, and the determination of G values for ammonia uptake and hexachloroethane production. An elemental analysis of the solid phase products had also revealed sizable quantitites of carbon containing compounds.

In the current investigation on the carbon tetrachloride-ammonia system, two things have been attempted. They are: (1) to obtain a complete product distribution, including product identification and measurement of yields; and (2) to obtain a more detailed knowledge of chemically reactive intermediates and of primary and secondary radiolytic processes.

SECTION II

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Apparatus

Vacuum Line

All samples of carbon tetrachloride and ammonia were prepared on the vacuum line shown in Figure 1. The pumping station for this high vacuum system was made up of a Welch Duo-Seal Model 1400B fore-pump, two liquid nitrogen cold traps, and a two stage mercury diffusion pump. By isolating pressure gauges (T) and (I) with a liquid nitrogen cold trap (N), pressure readings of 1×10^{-5} to 5×10^{-5} mm. could be obtained. Pressure measurements made without trapping were usually 8×10^{-5} to 2×10^{-4} mm. Attached to the main manifold were the following: a mercury manometer (M), an ammonia inlet with a barium oxide drying tube (D), two 50 ml. carbon tetrachloride reservoirs (R), ionization and thermocouple pressure gauges (I) and (T), a one liter ammonia storage reservoir (A), a 45.5 ml. calibrated volume (C), a combined McLeod gauge and Toepler pump (P) and a sub-manifold (S). To the sub-manifold, were attached 100 ml. and 10 ml. radiolysis vessels V_I and V_{II}. Stopcocks and standard taper joints were greased with Apiezon N and L vacuum greases.

Cobalt-60 Gamma Ray Source

All irradiations were carried out in a "Wisconsin" type Cobalt-60 gamma irradiator which has been described previously[8] (See also Figure 2).

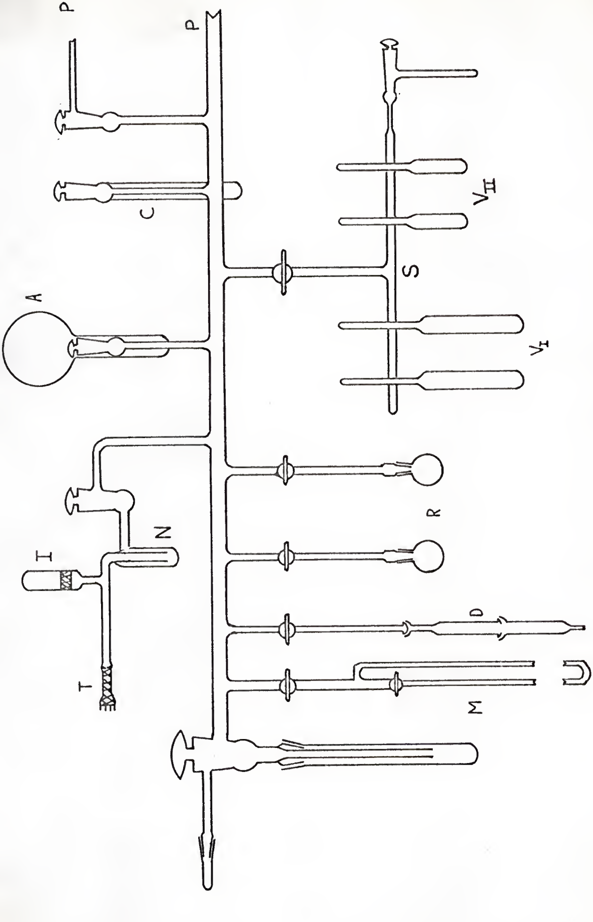
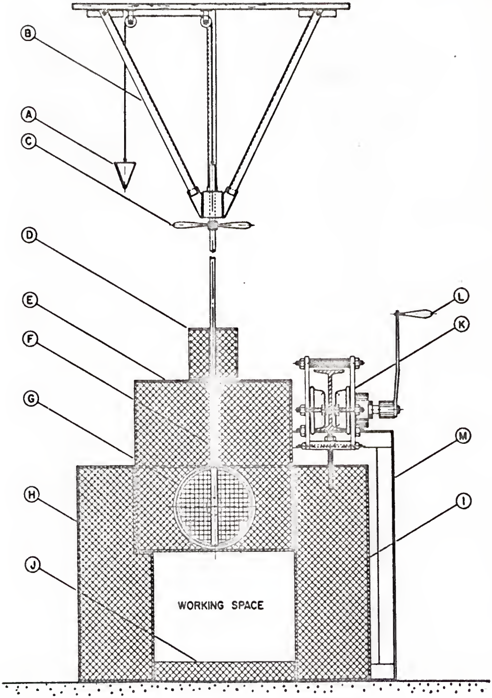


Figure 1. High Vacuum System.

Figure 2. Cross section of cobalt-60 gamma-ray source. Legend = (A) counterweight; (B) upper support; (C) control rod handle; (D) extra top shielding; (E) storage turret; (F) 400 curie Co^{60} source; (G) shutter shown open; (H) rear wall; (I) door: (J) downward shielding; (K) door carriage; (L) door crank; (M) door frame.


B
A
C
D
E
F
G
H
J
L
K
M
I
WORKING SPACE

Dose rates were measured relative to G(Fe^{+3}) of 15.6 for the Fricke dosimeter and corrected to dose absorbed in carbon tetrachloride using relative electron densities. Dose rates for the Fricke dosimeter on January 1, 1963, for 4, 25, and 300 ml. samples were .718, .412 and .406 x 10^{18} e.v./ml./min., respectively. All quantitative work was completed within one year of the above date. During this time interval, dose rates were corrected to take into account decay of the source. All irradiations were carried out at 25 ± 2°C. Radiolysis vessels and accompanying holders can be seen in Figure 3.

UV Light Source

The ultra-violet light source used in the photolysis experiments was a low pressure electrodeless mercury resonance lamp powered by a Raytheon model PGM-10 Microwave Generator using a type C antenna. The frequency and maximum power output of this generator were 2500 megacycles and 100 watts, respectively.

Figure 4 shows a full scale drawing of the mercury resonance lamp used in the present experiments. The main body of this light source was constructed from Pyrex tubing 20 mm. in diameter and 150 mm. in length. A ring seal at point (A) provided the lamp with a 34/45 male standard taper joint for making vacuum connections with various types of photolysis vessels. The optical window for this light source (B) consisted of a piece of Vycor tubing 20 mm. in diameter which was sealed off at one end and flattened. It was approximately 2 mm. in thickness. The window assembly was attached to the main body of the lamp by means of a Vycor to Pyrex graded seal (C). Tubulations (D) and (E) were designed to be used as a mercury storage well and a liquid nitrogen

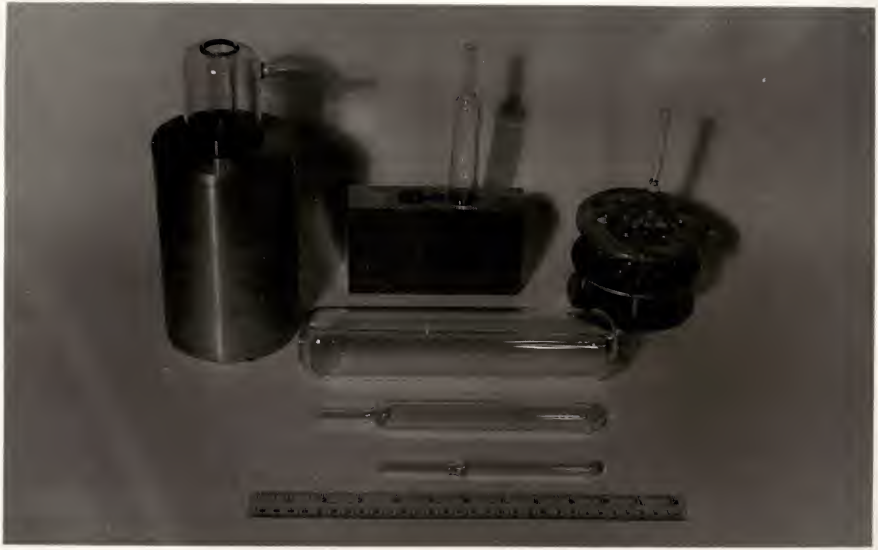


Figure 3. Radiolysis vessels and holders.

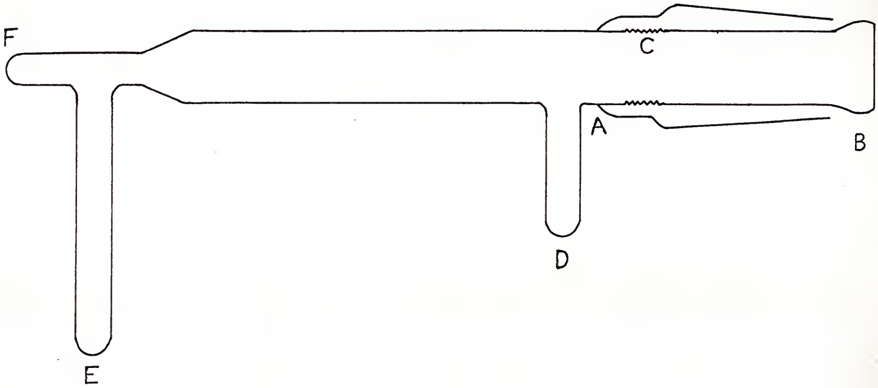


Figure 4. Electrodeless mercury-2537 resonance lamp.

cold finger. The cold finger served to remove unwanted water vapor and also helped to maintain a constant vapor pressure of mercury while the lamp was in operation.

The resonance lamp used in the photolysis experiments contained 75 mg. of mercury and was filled with 2 mm. pressure of argon. The argon tended to minimize mercury clean up and also increased the lamp's intensity somewhat. Conditioning of the lamp's glass surface was achieved by successive flushings with argon followed by the striking of a glow discharge. On the fourth filling the lamp was sealed off from the vacuum line at point (F).

The intensity of the UV light source at 2537 Å was determined using hydrogen bromide actinometry.[9] The quantum efficiency for the production of hydrogen for conversions of less than 1% has been given as 1.0. Photolysis of 500 mm. of hydrogen bromide with the lamp described above produced a hydrogen yield corresponding to an intensity of $3.6 \pm .3 \times 10^{16}$ quanta/sec.

Bendix Time-of-Flight Mass Spectrometer

The mass spectrometer used in the ion-molecule and fast flow studies was a Bendix model 14-107 Time-of-Flight instrument, having a mass resolution of 270. The machine used in the present investigation together with its supporting equipment can be seen in Figure 5. The essential features of the Time-of-Flight mass spectrometer are shown in Figure 6.

For the ion-molecule studies a special high pressure ion source was purchased from the Bendix Corporation. Using a Heraeus four inch oil diffusion pump for differential pumping, data was collected up to a

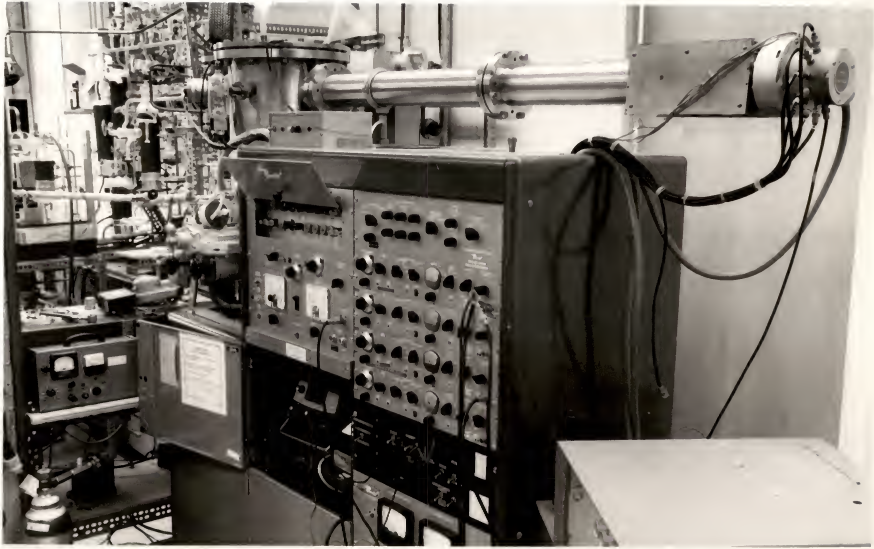


Figure. 5. Bendix Model 14-107 Time-of-Flight Mass Spectrometer and auxillary equipment.

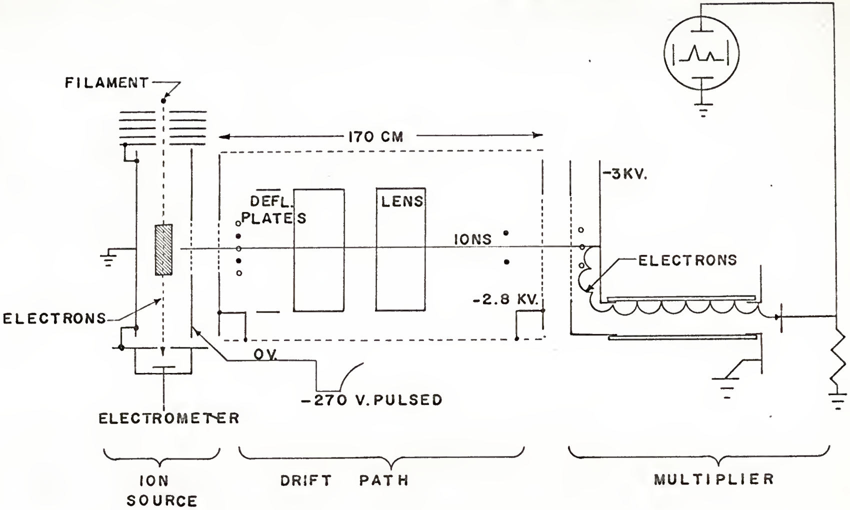


Figure 6. Schematic of Bendix Time-of-Flight Mass Spectrometer.

pressure of 80 microns; however, the resolution at pressures above 35 microns ranged only from poor to fair. During these investigations the machine was operated in a pseudo Studier mode--ion generation, pulsed and electron beam, continuous.*

Fast Flow Apparatus

The basic elements of the fast flow apparatus used in the present investigation (see Figure 7) were as follows: two sample reservoirs (R_C) and (R_A), a fast flow reaction tube (F), a microwave source (M), three sample inlet tubes (I), a sampling port (S), a detector (D), a pressure gauge (P), and a liquid nitrogen cold trap (C).

The Raytheon microwave unit used in these experiments was the same one described under the heading "UV Light Source." The Pyrex fast flow reaction tube had an I.D. of 11 mm. and a total length from position V to the sampling port of 70 cm. The end of the tube was approximately 2 mm. from the sampling port. The details of how the flow tube was connected to the fast reaction chamber of the mass spectrometer can be seen in Figure 8.

During an experiment, the microwave antenna was usually placed at one of the five positions shown in Figure 7. With a measured flow rate of 10 m/sec., minimum and maximum residence times were of the order of 35 and 70 milliseconds, respectively.

The pressure in these experiments was monitored with a Baratron capacitive pressure gauge which has an operational range of .1 to 3,000 microns. The pressure was regulated by means of Teflon needle valves;

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*For a more complete explanation of the various modes of operation of the Bendix Time-of-Flight Mass Spectrometer see reference (10).

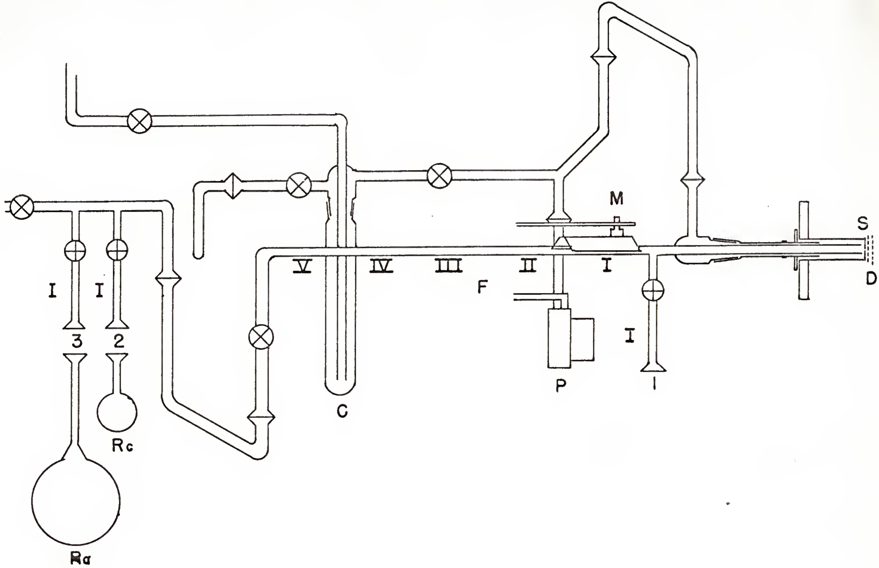

Figure 7. Fast flow system.

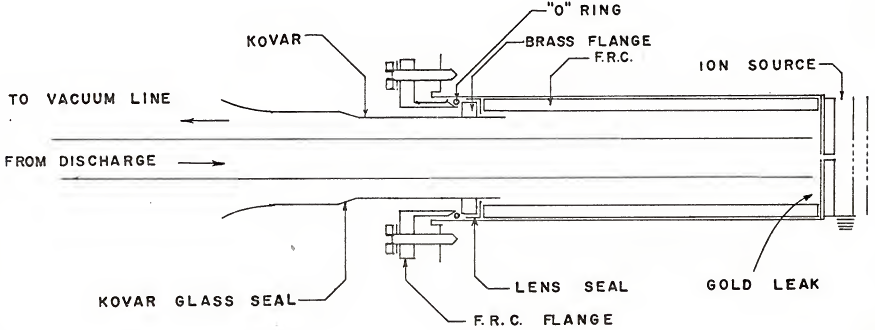

Figure 8. Details of connection between flow tube and fast reaction chamber of the mass spectrometer.

however, additional control was obtained by immersion of the sample reservoirs in appropriate low temperature baths. A dry ice and carbon tetrachloride slush was used in the case of carbon tetrachloride, and dry ice and acetone was used for ammonia.

The sample reservoirs could be attached to the flow system at any one of three possible positions, depending on the type of experiment being carried out. For mixture experiments sample reservoirs were located at inlets 2 and 3, whereas, in so called downstream studies one reservoir was at position 2 and the other at position 1.

The Bendix Time-of-Flight mass spectrometer, which was used as a detector in these experiments, was operated in its normal mode--ion generation, pulsed and electron beam, pulsed.

Reagents

Ammonia

All experiments were carried out using Matheson Company reagent grade ammonia.

Carbon Tetrachloride

"Baker Analyzed" reagent grade carbon tetrachloride was used without further purification.

Preparation of Samples

Radiolysis

To a round-bottomed flask containing 4, 25, or 300 ml. of carbon tetrachloride (R), 1 g. of barium oxide was added for each 5 ml. of sample. The flask was attached to the main manifold of the vacuum system shown in Figure 1 by a ground-glass joint, and the mixture was degassed by four cycles of the freeze-evacuate-melt technique. Ammonia was dried by passage through a column of powdered barium oxide (D) and stored in a 1 liter bulb (A) attached to the main manifold. It was then degassed in the same manner as carbon tetrachloride. After degassing, carbon tetrachloride was vacuum distilled into pyrex irradiation vessels (V_I or V_{II}). Ammonia was added to these vessels as follows: the gas was admitted to the main manifold until a pressure of approximately 80 cm. was obtained; a calibrated volume of 45.5 ml. (C) was trapped off from the manifold, and the excess ammonia was frozen down in the storage bulb; transfer from the calibrated volume to the irradiation vessel was then made directly. The number of aliquots of ammonia transferred depended upon the volume of carbon tetrachloride to be irradiated. In all cases a sufficient amount of ammonia was added to insure that the concentration of the solution was about .2 M. After completion of the ammonia transfer the vessel was sealed off under vacuum and brought up to room temperature.

Photolysis

Sample preparation in the photolytic experiments was very similar to that described above for the radiolysis investigations. In the case of the photolysis samples, however, a high vacuum line was used which employed an oil diffusion pump rather than mercury. This was necessary in order to minimize mercury photo-sensitization reactions. The photolysis vessel used in these experiments was a Vycor tube 20 mm. in diameter fitted with a Vycor to Pyrex graded seal. In a typical run this vessel would be filled with 10 ml. of carbon tetrachloride-ammonia solution. All photolysis experiments were carried out at 25 ± 2°C.

Product Analysis

Solid Phase

Qualitative analyses of the solid phase products were made using thin layer and ion-exchange chromatography and infrared and ultraviolet spectrophotometry.

To develop a thin layer chromatography procedure applicable to the carbon tetrachloride-ammonia system, a wide variety of adsorbents, solvents, and detection reagents were tested. A list of these materials is given in Table II.

Of the many different combinations of adsorbent, solvent, and developing reagent that were tried, the one that was most satisfactory was MN-300-HR cellulose, MeOH/PrOH/H_2O (40:40:20), and $AgNO_3$.

All thin layer chromatography (TLC) work was done using 10 x 20 cm. glass plates. Since the MN-300-Hr cellulose contained no $CaSO_4$ binder, it was most important that all glass surfaces to be coated were completely free of scratches.

Cellulose coatings on TLC plates were normally either .3 or 1 mm. thick. To prepare two plates 1 mm. in thickness, 14 g. of MN-300-HR cellulose was mixed with 70 ml. of distilled water and the mixture stirred vigorously for 15 minutes using a hand held electric mixer. The slurry was then poured into the hopper of a "Camag" spreader and two plates were rapidly pushed through with a third plate serving as a back up. Upon drying overnight at room temperature the plates were ready for use.

For qualitative work the size of the sample ranged from 3 to 100 mg. In a normal operation the sample was taken up in .5 ml. of

TABLE II

TLC MATERIALS

Adsorbents[a]	Solvents[b]	Detection Reagents
Silica Gel G	MeOH	Conc. H_2SO_4
Aluminum Oxide G	MeOH/PrOH (50:50)	I_2
MN-300G Cellulose	MeOH/PrOH/H_2O (47:47:6)	Starch, KI
MN-300-HR Cellulose	MeOH/PrOH/H_2O (45:45:10)	$AgNO_3$
MN-300-GF Cellulose	MeOH/PrOH/H_2O (40:40:20)	

[a] All adsorbents listed above were purchased from the Brinkman Co.

[b] Volume ratio.

methanol and transferred to the TLC plate in the form of a band. Plates were presaturated in a vertical ascending developing chamber for 30 minutes using the solvent mixture described earlier, MeOH/PrOH/H_2O (40:40:20). Additional solvent was then added until the developing process was initiated. Developed plates were dried, and approximately one-fourth of the surface of each plate was sprayed with a $AgNO_3$ solution to make the separated compounds visible. R_f values were then determined for these bands and compared with those of pure organic nitrogen compounds. By making simple extrapolations across the plate, unsprayed cellulose bands containing radiolysis products could also be located. These bands were removed and the compounds within them were extracted with water. Ultraviolet spectra were run on the filtered extracts without further manipulation. In order to obtain a sufficient amount of sample for infrared spectra, bands from ten or more TLC plates were usually required.

Ion-exchange chromatography was used to obtain both qualitative and quantitative data on the compounds cyanoguanidine, guanidine hydrochloride, and ammonium chloride. To analyze quantitatively for these compounds, 100 mg. of radiolysis sample was taken up in 50 ml. of water and added to a Dowex 50W-X8 ion-exchange column 1.45 cm. in diameter and 37 cm. high. Approximately 400 ml. of distilled water was passed through the column at a flow rate of 4 ml./min. and the collected effluent was then made up to a total volume of 500 ml. Analysis of cyanoguanidine was made by adding 100 ml. of the stock solution to a Rexyn I-300 (H-OH) strong cation-anion-exchange column 2.5 cm. in diameter and 6.0 cm. high. After 250 ml. of distilled water had been passed through this column (again at a rate of 4 ml./min.), the optical density of the effluent was recorded at the $\lambda_{max.}$ for cyanoguanidine, 212.5 mμ, on a Beckman DU spectrophotometer ($\epsilon = 1.37 \times 10^4 M^{-1} cm.^{-1}$). Estimated error ± 4%.

Ammonium and guanidinium ions were removed sequentially from the Dowex 50W-X8 ion-exchange column with 300 ml. of 1 N and 200 ml. of 6N HCl. Three Kjeldahl nitrogen determinations were made on each of the above column fractions. Estimated error ± 5%.

Analysis of ammonium dicyanamide involved a combination of thin layer chromatography and ultraviolet spectrophotometry. Normally 25 mg. of radiolysis mixture was transferred to a cellulose TLC plate, and the plate was developed in the same manner as described earlier. After drying, the cellulose band containing ammonium dicyanamide was removed and the ammonium dicyanamide was extracted with 50 ml. of water. Finally, the optical density of the solution was recorded at 215 mμ (a shoulder in the ammonium dicyanamide ultraviolet spectra, $\epsilon = 1.25 \times 10^3 M^{-1} cm^{-1}$) on a Beckman DU spectrophotometer. Estimated error ± 10%.

Liquid Phase

Both qualitative and quantitative analyses of the liquid phase products hexachloroethane and chloroform were preformed by gas chromatography. Irradiated samples were separated on a glass column six feet in length, .25 inches in diameter, and packed with silicone gum rubber on Chromosorb-W. The detector was of the flame ionization type. Estimated error ± 5%.

Hydrazine, another possible liquid phase product, was analyzed for by measuring spectrophotometrically the amount of potassium permanganate reduced in a previously added known volume of standardized solution.

Before the addition of the permanganate solution to the irradiated sample, care was taken to remove any unreacted ammonia by vigorous stirring and slight heating. This method was sufficiently sensitive as to be able to detect hydrazine yields of the order of one-tenth of a G value unit. Estimated error ± 10%.

Gas Phase

To analyze for gas phase radiolysis products, irradiated samples equipped with break seals were attached to the high vacuum line shown in Figure 7 and opened at -196°C. The noncondensable materials were collected via a Toepler pump and the gas pressure measured on a McLeod gauge (each sample was degassed approximately seven times). The collected gas samples were analyzed on a Consolidated 20-130 mass spectrometer. Estimated error ± 5%.

SECTION III

EXPERIMENTAL RESULTS AND DISCUSSION

Products from the Gamma Radiolysis of Carbon Tetrachloride-Ammonia Solutions

Solid Phase

In Figure 9 the total yield of solid phase products is shown plotted as a function of the energy absorbed by the system. From this plot it can be seen that the solid phase product yield is directly proportional to the energy absorbed up to a dose of 1.25×10^{20} e.v./g. Infrared and ultraviolet spectra of the untreated solid phase product mixture are shown in Figures 10 and 11. (Table III lists several characteristic infrared absorption bands commonly found in nitrogen containing compounds.)[11]

Figures 12 and 13 show the results from thin layer chromatographic analyses of the radiolysis mixture. In the first figure the compounds cyanoguanidine, guanidine hydrochloride, and ammonium chloride together with the radiolysis mixture are shown separated on a TLC plate which was developed in the solvent mixture MeOH/PrOH/H_2O (45:45:10). Approximately .1 mg. of each compound was deposited on the TLC plate in this analysis. The second figure depicts the separation of 15 mg. of solid phase radiolysis products on a cellulose TLC plate developed in MeOH/PrOH/H_2O (40:40:20) solvent. The bands on the left have been made visible by spraying with $AgNO_3$ solution, whereas, those on the right fluoresce under an ultraviolet mineral lamp (band areas are not necessarily proportional to

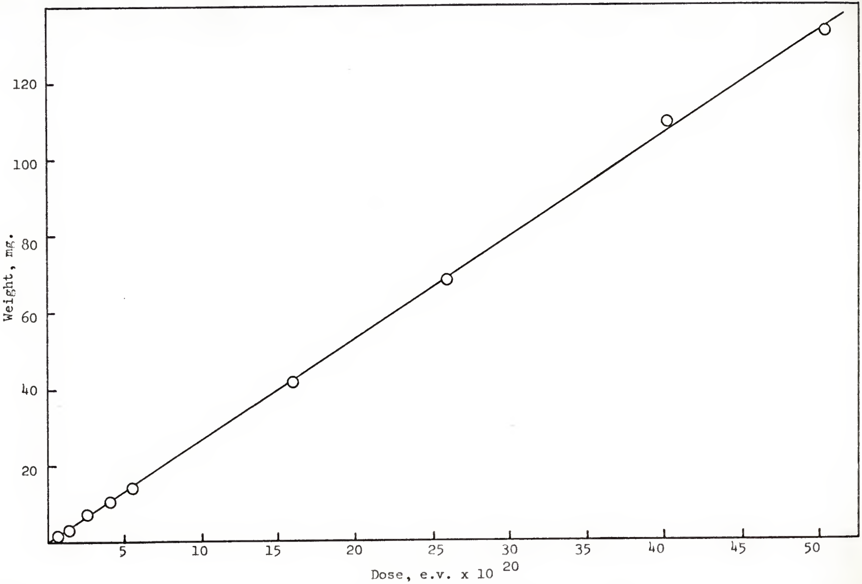

Figure 9. Total yield of solid-phase products as a function of radiation dose.

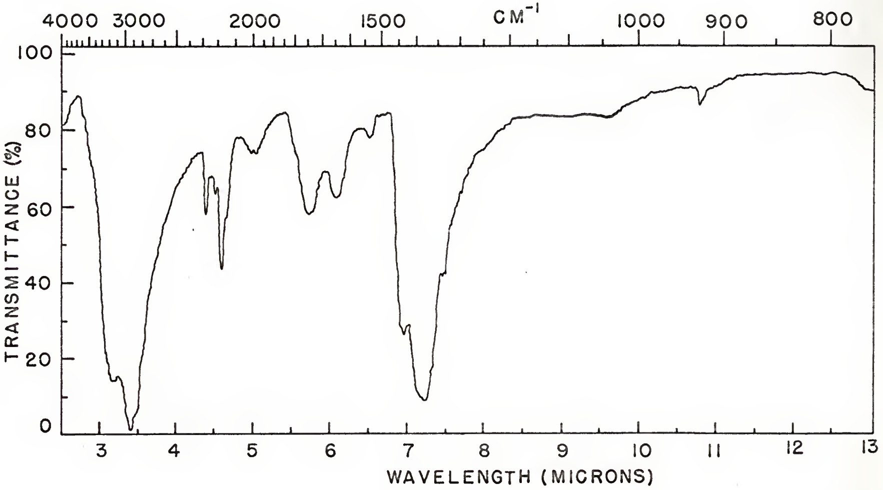

Figure 10. Infrared absorption spectrum (nujol mull) of the untreated solid phase product mixture.

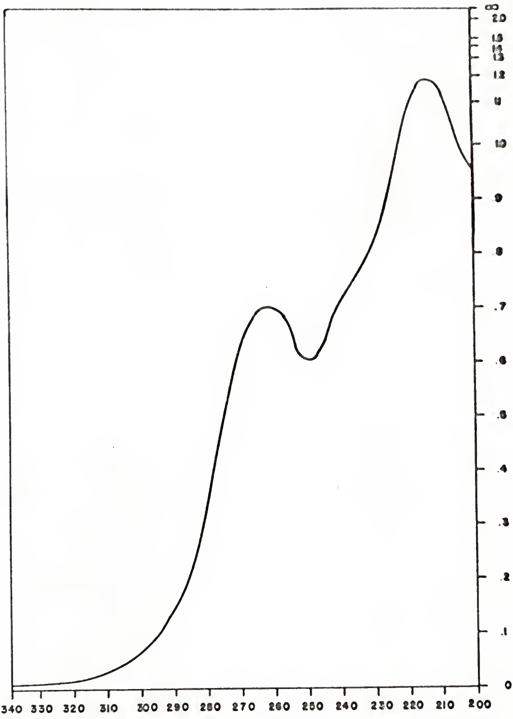

Figure 11. Ultraviolet absorption spectrum of the untreated solid phase product mixture--dilute aqueous solution.

TABLE III

CHARACTERISTIC INFRARED ABSORPTION BANDS

Nature of Vibration		Wavelength Range
*st	NH	2.94-3.00
st	NH_2	2.88-3.24
st	NH_4	3.10-3.28
st	C=N	4.31-5.25
st	C=N	5.94
d	NH_2	5.95-6.39
d	NH_4	7.00-7.40
w,r	NH_2	8.90
st	CN	7.19-11.89
st	CNC	10.75-11.19
t	NH_2	13.35
b	CN	14.04

*st = streching, d = deformation, w = wagging, r = rocking, t = twisting, b = bending.

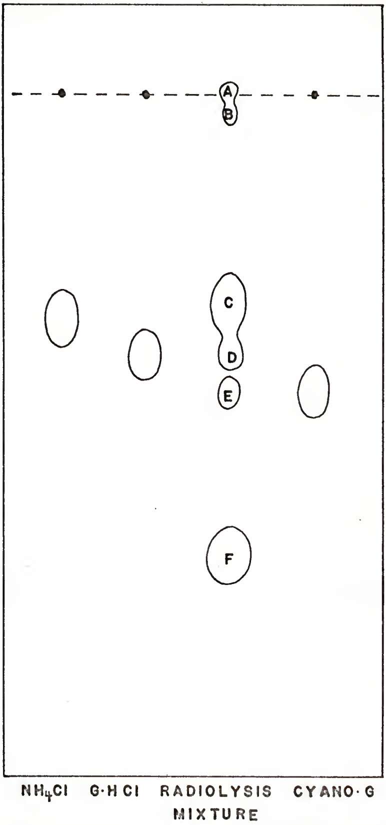

Figure 12. Reproduction of a developed cellulose TLC plate showing the separation of .1 mg. of cyanoguanidine, guanidine hydrochloride, ammonium chloride, and radiolysis mixture.

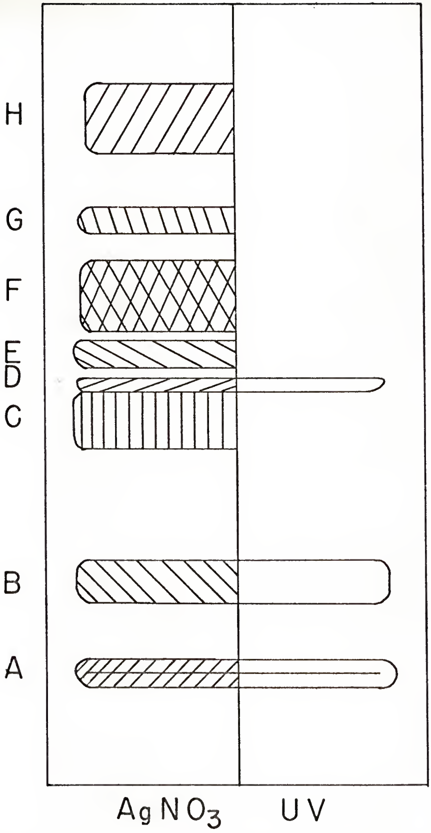

Figure 13. Sketch of a developed cellulose TLC plate showing the separation of 15 mg. of solid phase radiolysis products.

the amount of compound present). Infrared and ultraviolet spectra of the compounds extracted from these bands are shown in Figures 14 through 20. For comparison, infrared and ultraviolet spectra of some commercially obtained nitrogen compounds appear in Figures 21 through 25. It was on the basis of these spectra, together with the TLC results shown in Figure 12, that the following assignments were given to the TLC bands appearing in Figure 13:

Band A - Unknown, fluorescence activity and ultraviolet spectrum indicate the presence of a delocalized pi electron system, possibly a triazine compound.

Band B - Unknown, the above comments also apply to this compound.

Band C - Unknown, no information available.

Band D - Unknown, similar to compounds in bands A and B.

Band E - Unknown, the long wavelength absorption of this compound again indicates a high degree of electron delocalization.

Band F - Ammonium chloride plus guanidine hydrochloride.

Band G - Cyanoguanidine.

Band H - Ammonium dicyanamide.

The four solid phase radiolysis products identified above accounted for 98 per cent (by weight) of the radiolysis mixture.

Figures 26 through 29 show product yield curves for the compounds cyanoguanidine, guanidine hydrochloride, ammonium chloride, and ammonium dicyanamide. It can be seen from these plots that all four compounds show a linear relationship between yield and energy absorbed at doses

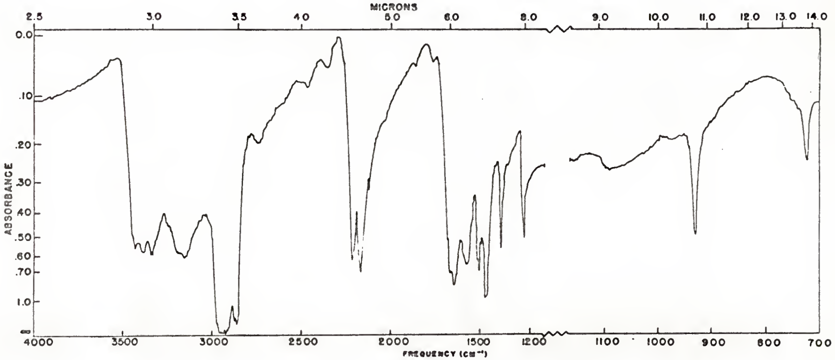

Figure 14. Infrared absorption spectrum (nujol mull) of the radiolysis product in band G.

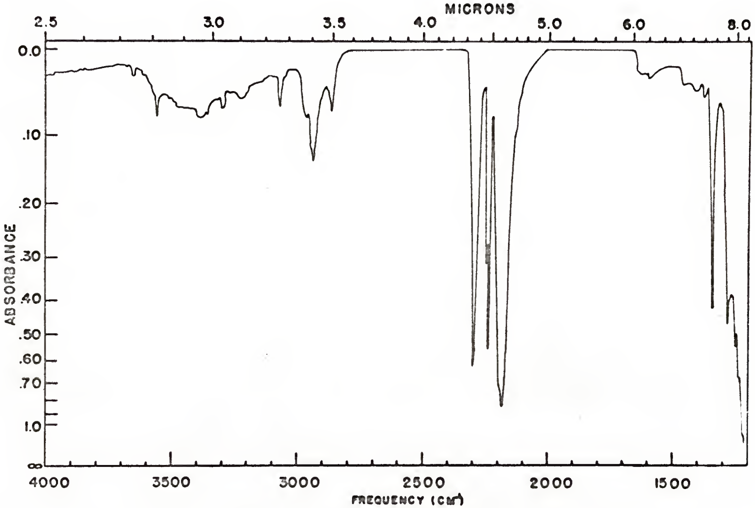

Figure 15. Infrared absorption spectrum (nujol mull) of the sodium salt of the radiolysis product in band H.

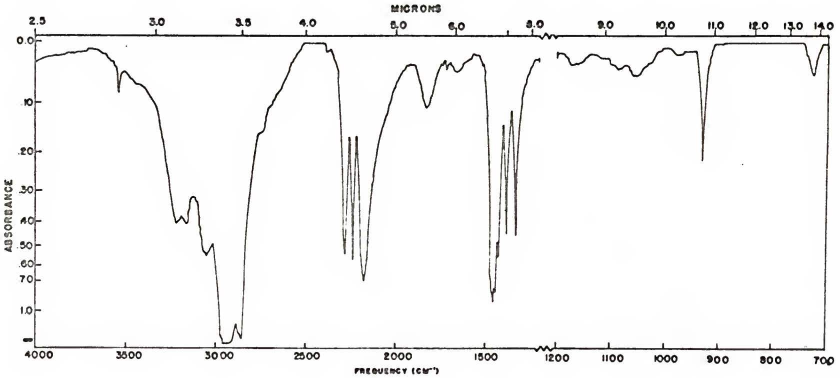

Figure 16. Infrared absorption spectrum (nujol mull) of the radiolysis product in band H.

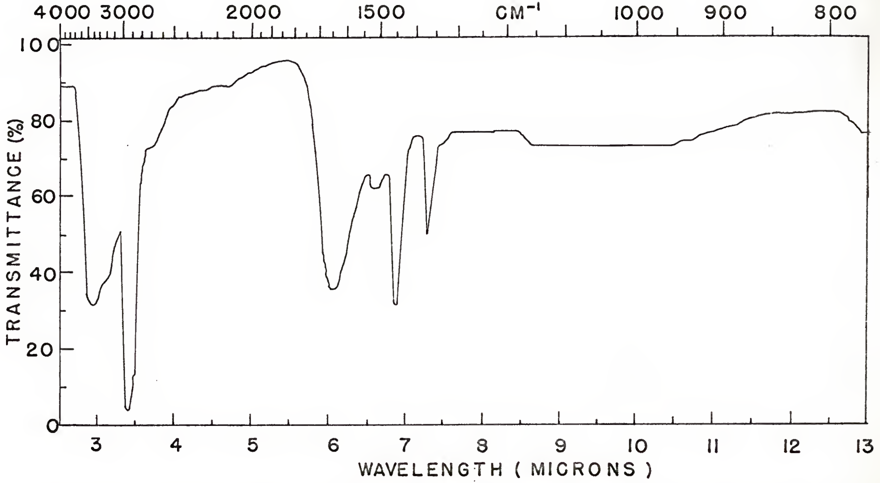

Figure 17. Infrared absorption spectrum (nujol mull) of one of the radiolysis products in band F.

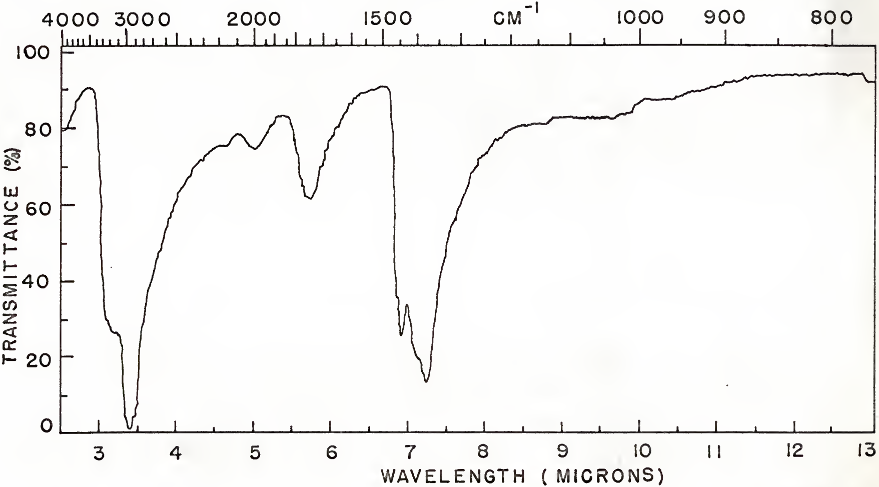

Figure 18. Infrared absorption spectrum (nujol mull) of a second radiolysis product in band F.

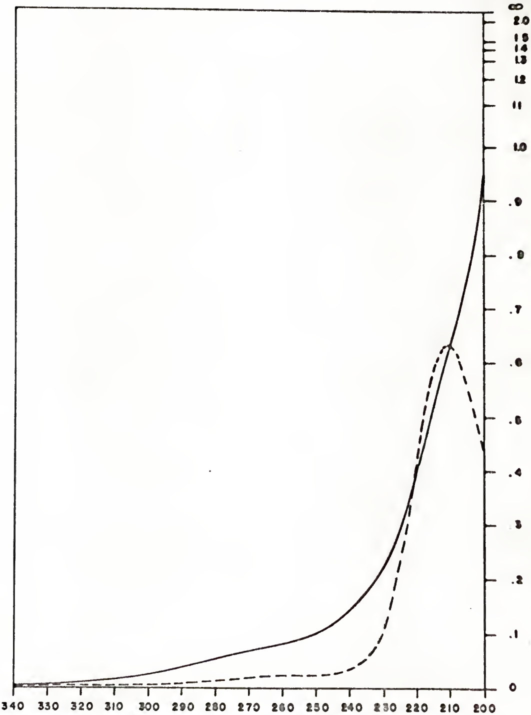

Figure 19. Ultraviolet absorption spectra of radiolysis products in bands H and G. Dash curve = band G, solid curve = band H. Samples were run in aqueous solution.

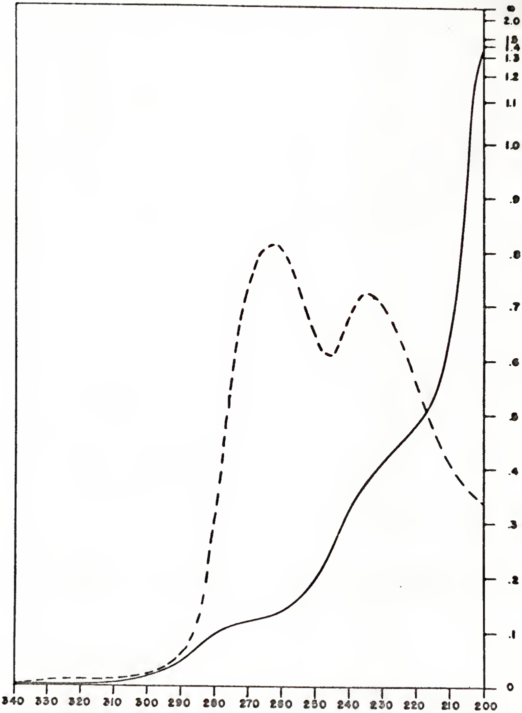

Figure 20. Ultraviolet absorption spectra of radiolysis products in bands A and E. Dash curve = band E, solid curve = band A. Samples were run in aqueous solution.

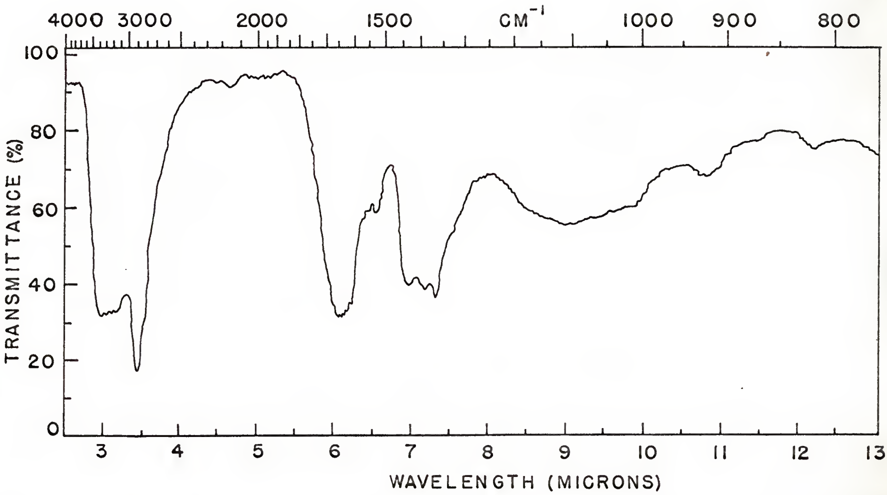

Figure 21. Infrared absorption spectrum (nujol mull) of guanidine hydrochloride.

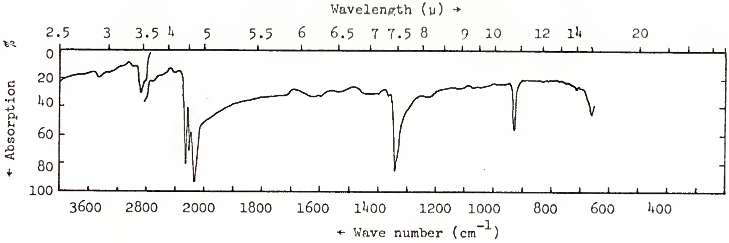

Figure 22. Infrared absorption spectrum (nujol mull) of sodium dicyanamide.

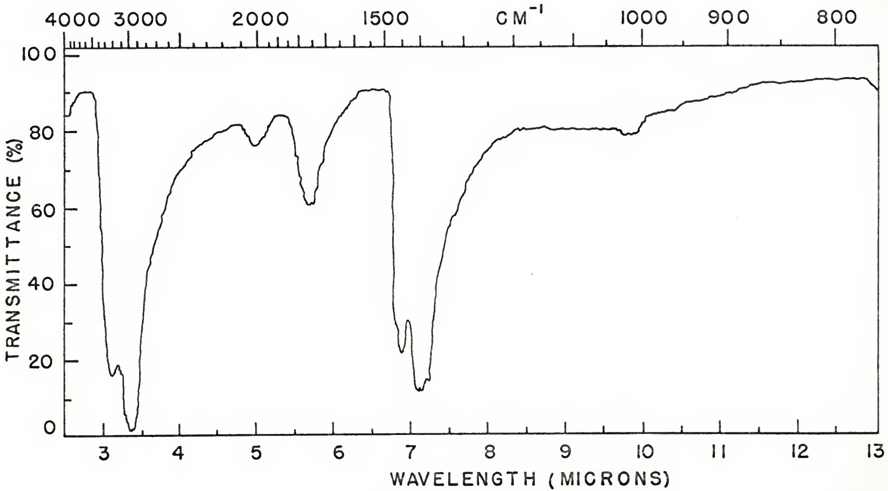

Figure 23. Infrared absorption spectrum (nujol mull) of ammonium chloride.

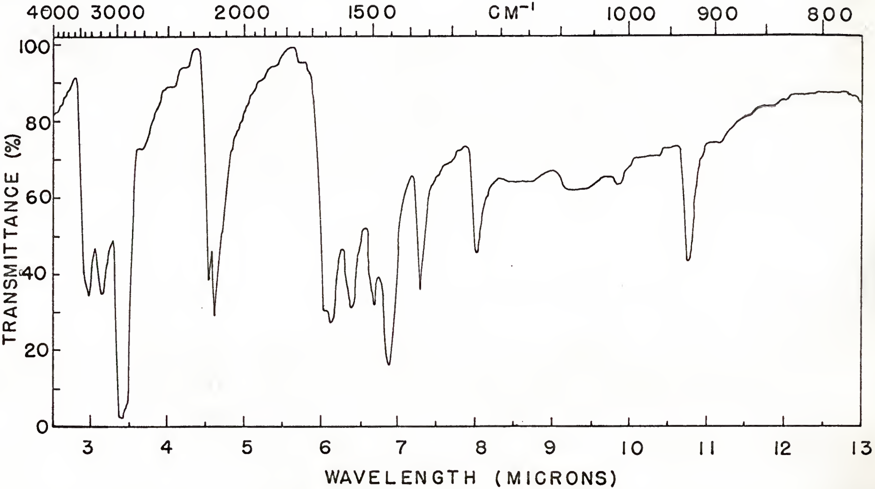

Figure 24. Infrared absorption spectrum (nujol mull) of cyanoguanidine.

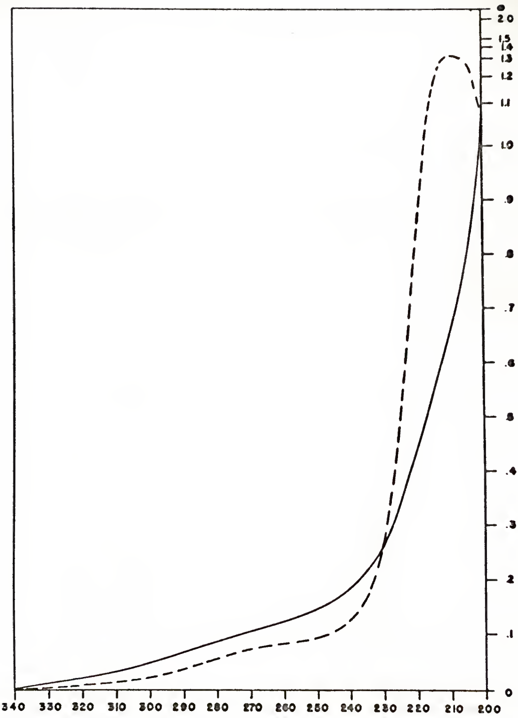

Figure 25. Ultraviolet absorption spectra of cyanoguanidine and ammonium dicyanamide. Dash curve = cyanoguanidine, solid curve = ammonium dicyanamide. Samples were run in aqueous solution.

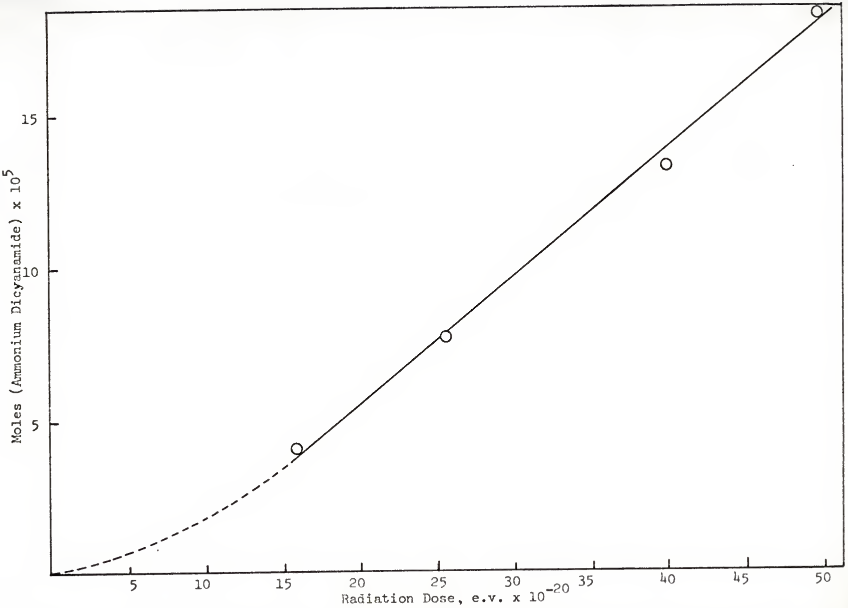

Figure 26. Formation of ammonium dicyanamide as a function of radiation dose.

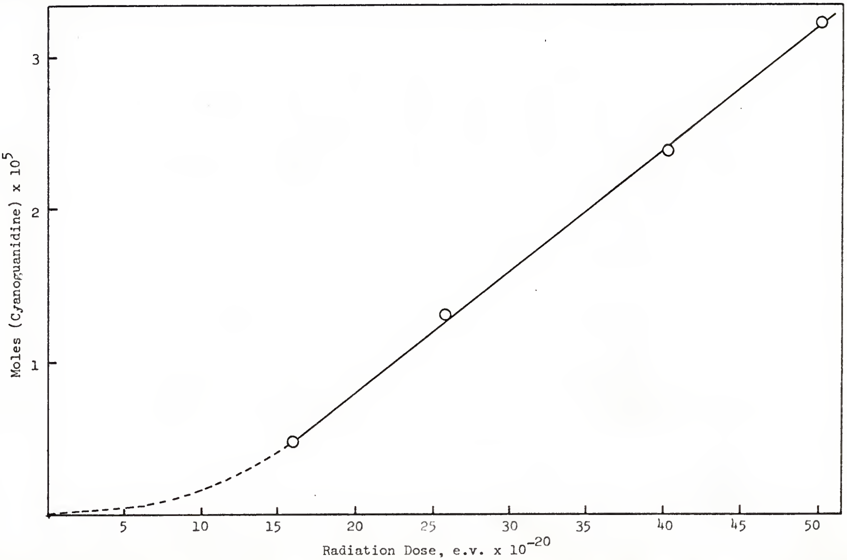

Figure 27. Formation of cyanoguanidine as a function of radiation dose.

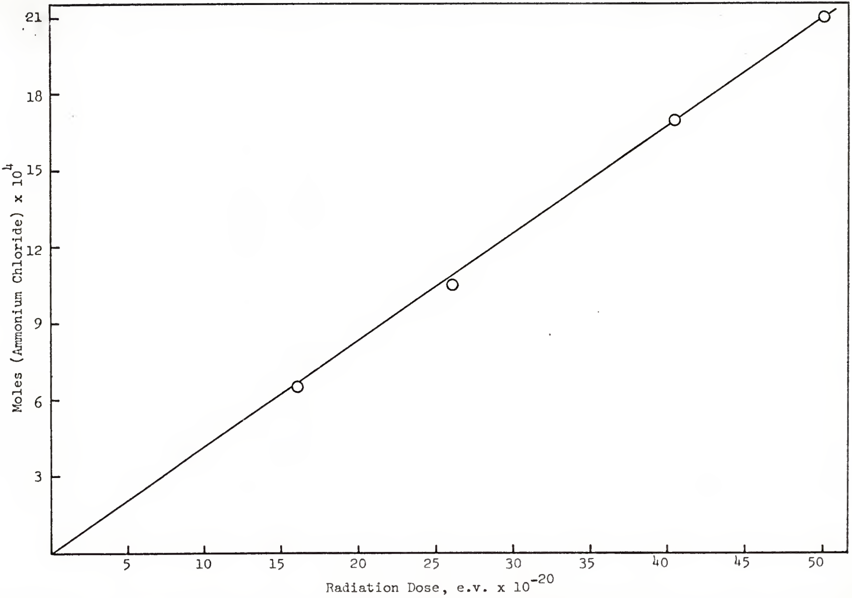

Figure 28. Formation of ammonium chloride as a function of radiation dose.

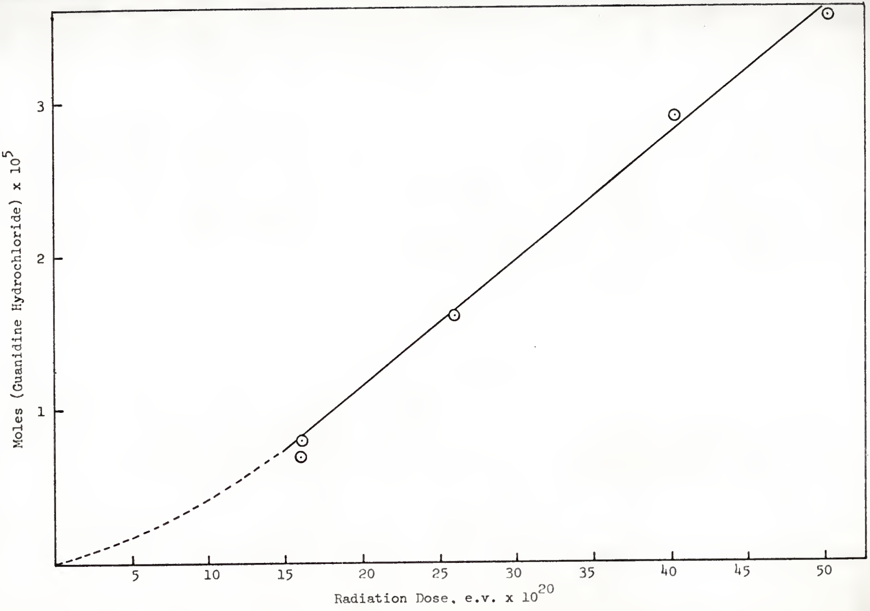

Figure 29. Formation of guanidine hydrochloride as a function of radiation dose.

greater than 15×10^{20} e.v. Only the ammonium chloride curve, however, extrapolates through the origin. The induction period observed for the organic nitrogen products would suggest that these compounds are formed via some chemically reactive intermediate.

G values for the compounds cyanoguanidine, guanidine hydrochloride, ammonium dicyanamide, and ammonium chloride were found to be .48, .53, 2.36, and 25.3, respectively. These values were obtained by measuring the slopes of the product yield curves over those regions where the yields were a linear function of the energy absorbed.

Liquid Phase

A plot of hexachloroethane production as a function of dose is shown in Figure 30. The G value for this compound was 2.13. This value was found to be independent of total dose up to 6×10^{20} e.v.

Analysis of the liquid phase for chloroform and hydrazine showed that these compounds are formed with G values of less than .1.

Loss of ammonia during radiolysis was measured in the liquid phase by direct titration with standardized sodium hydroxide. (These data were obtained by Mr. James Buchanan.)[12] At a total dose of 5×10^{20} e.v., values for $G(-NH_3)$ ranged from 35.6 to 39.3.

Gas Phase

In Figure 31 the yield of molecular nitrogen is plotted against energy absorbed. Above a dose of 5×10^{20} e.v., the G value for nitrogen formation was constant at .80. Analysis of the noncondensable gas phase radiolysis products by mass spectrometry revealed that 96% of the gas mixture was nitrogen and 4% was hydrogen. Thus, $G(H_2)$ is less than .1.

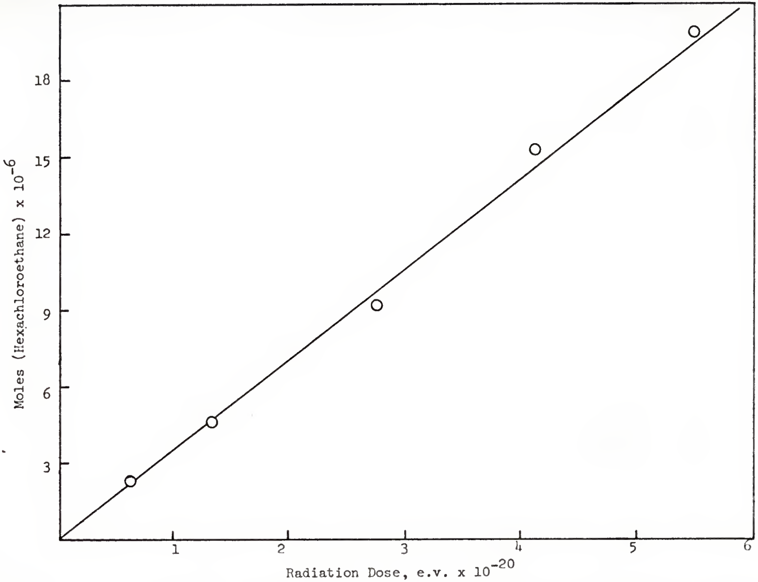

Figure 30. Formation of hexachloroethane as a function of radiation dose.

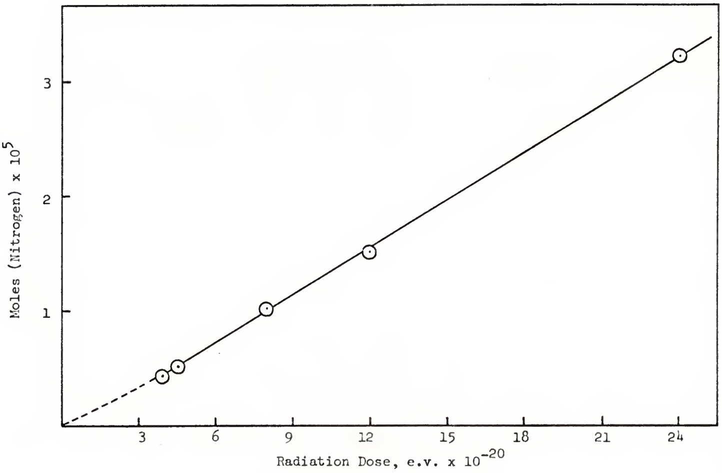

Figure 31. Formation of nitrogen as a function of radiation dose.

Material Balance

Table IV gives a material balance for the elements carbon, hydrogen, chlorine, and nitrogen expressed as G values. The purpose of this table is to show that the reported product yields are internally consistent. That this is the case can be seen by examining the ratios of chlorine to carbon and of hydrogen to nitrogen. The respective values for these ratios are 3.69 and 2.90, compared to the expected values of 4 and 3. An additional check can be made by comparing G(N) with $G(-NH_3)$. The latter quantity has a value ranging from 35.6 to 39.3; in good agreement with this, G(N) equals 39.8. Another piece of information available from Table IV is the value of G(C-Cl). Since in all radiolysis experiments the percent conversion of carbon tetrachloride to product was limited to less than 2%, G(C-Cl) can be equated directly to G(C) or 10.5.

Discussion

Since the radiolysis system investigated in the present work consisted of binary mixtures of carbon tetrachloride and ammonia, the radiolysis yield might be expected to consist of products from pure carbon tetrachloride and from pure ammonia, as well as mixed products derived from both starting materials. One of the major products from carbon tetrachloride, namely hexachloroethane, was found in substantial amounts. The formation of the other product, chlorine, was not anticipated because of its reactivity toward ammonia, and it was not found. The products which might result from ammonia include nitrogen, hydrogen, and hydrazine. Only one of these compounds, nitrogen, was found in appreciable yield. Its mode of formation will be discussed shortly.

TABLE IV

YIELDS AND MATERIAL BALANCE

Product	G Values	H	Cl	C	N
C_2Cl_6	2.13	0	12.78	4.26	0
Guanidine·HCl	0.53	3.18	0.53	0.53	1.59
Cyanoguanidine	0.48	1.92	0	0.96	1.92
Ammonium Dicyanamide	2.36	9.44	0	4.72	9.44
NH_4Cl	25.3	101.2	25.3	0	25.3
N_2	0.80	0	0	0	1.60
		115.74	38.61	10.46	39.85

H/N = 2.90

Cl/C = 3.69

Among the products derived from both starting materials were ammonium chloride, ammonium dicyanamide, cyanoguanidine, and guanidine hydrochloride. It should be noted that several radiolysis products contained cyano groups, suggesting that a common precursor might be involved, and that the ammonium chloride yield was so large (G = 25.4) that it could not arise directly from a single radiolysis step. All of these observations are consistent with the following sequence of reactions.

$$CCl_4 \rightarrow \cdot CCl_3 + Cl\cdot \tag{1}$$

$$\cdot CCl_3 + \cdot CCl_3 \rightarrow C_2Cl_6 \tag{2}$$

$$Cl\cdot + NH_3 \rightarrow HCl + \cdot NH_2 \tag{3}$$

$$\hookrightarrow NH_3 \rightarrow NH_4Cl$$

$$\cdot CCl_3 + \cdot NH_2 \rightarrow NH_2CCl_3 \tag{4}$$

$$NH_2CCl_3 \rightarrow Cl_2C{=}N{-}H + (HCl)^a \tag{5}$$

$$Cl_2C{=}N{-}H \rightarrow Cl{-}C{\equiv}N + (HCl) \tag{6}$$

$$Cl{-}C{\equiv}N + NH_3 \rightarrow NH_2C{\equiv}N + (HCl) \tag{7}$$

$$NH_2C{\equiv}N + Cl{-}C{\equiv}N \rightarrow H{-}N(CN)_2 + (HCl) \tag{8a}$$

$$\llcorner\!\!-\!\!-\ NH_3 \rightarrow NH_4{}^{+}N(CN)_2^{-}$$

$$NH_2C{\equiv}N + NH_3 \rightarrow (NH_2)C{=}NH \tag{8b}$$

$$\llcorner\!\!-\!\!-\ (HCl) \rightarrow (NH_2)C{=}NH_2^{+}Cl^{-}$$

$$NH_2C{\equiv}N + NH_2C{\equiv}N \rightarrow (NH_2)C{=}N{-}C{\equiv}N \tag{8c}$$

From the proposed reaction scheme it can be seen that several moles of ammonium chloride are produced for each mole of carbon tetrachloride consumed. For example, in the formation of one mole of

---

[a] The parentheses indicate that HCl is not produced as such but rather taken up by ammonia. Ammonia, in fact, is probably involved either stoichiometrically or catalytically in most of the above mechanistic steps beyond reaction 3.

ammonium dicyanamide, eight moles of ammonium chloride are formed as a by-product. Hence, the large G value of ammonium chloride does not indicate a chain process but merely reflects the stoichiometry of the reaction.

Additional evidence supporting the suggested reaction scheme can be found in some synthetic work carried out by Ascher.[13] Ascher reported synthesizing trichloromethylamine, the reactive intermediate formed in reaction 4, and found that the compound was strongly acidic because of the inductive effect of the chlorine atoms. Reactions 5 and 6 are in keeping with these observations.

Reactions 7 through 8c suggest that it is the formation of the intermediates cyanogen chloride and cyanamide that result in the observed induction periods for the organic nitrogen compounds. The presence and relative extent of these induction periods follow from the fact that steady-state concentrations of cyanogen chloride and cyanamide must first be established before reactions 8a-c can give maximum yields of stable products. Since the ammonia concentration was nearly constant during the experiments for which quantitative yield data was taken, the constant yields of the products of reactions 8a-c must reflect constant steady-state concentrations of cyanogen chloride and cyanamide. An approximation of the respective steady-state concentrations of these two intermediates can be calculated with the help of Figures 26 and 27. In the case of cyanogen chloride, the steady-state concentration would correspond to the onset of a constant G value for the yeild of ammonium dicyanamide. Using the equation:

$$G(\mathrm{ClCN})_{\mathrm{max.}} = 2G(\mathrm{NH_4^+N(CN)_2^-})_{\mathrm{const.}} = \frac{\#\mathrm{moles\ ClCN} \times 100}{\mathrm{total\ dose\ (t)} \times 6.02 \cdot 10^{23}},$$

where the total dose at time (t) refers to the time required to attain a constant yield of ammonium dicyanamide, the number of moles of cyanogen chloride at a time (t) or greater was calculated to be $8.6 \cdot 10^{-5}$, or for 25 ml. of solution a concentration of 3.4×10^{-4} M. Using a similar equation but with G of cyanoguanidine replacing G of ammonium dicyanamide, the concentration of cyanamide was found to be $1 \cdot 10^{-3}$ M. Since ammonium dicyanamide was the major organic nitrogen product in the radiolysis mixture, it must be concluded that reaction 8a is the most rapid under the present experimental conditions.

The small yield of hydrazine among the liquid phase products and the moderately high G value for nitrogen in the gas phase seems to indicate that hydrazine is being consumed by secondary reactions. A likely process would be hydrogen abstraction by NH_2 radicals,[14,15] e.g.

$$\cdot NH_2 + N_2H_4 \rightarrow NH_3 + \cdot N_2H_3$$

$$2N_2H_3\cdot \rightarrow 2NH_3 + N_2$$

This sequence of reactions would also explain the fact that although $G(N_2) = .80$, the G value for hydrogen was less than .1.

Review

It has been shown from the analytical work that the major products formed in the gamma radiolysis of carbon tetrachloride and ammonia solutions are ammonium dicyanamide, ammonium chloride, and hexachloroethane. The reaction scheme, 1 through 8c, accounts for the formation of these products in terms of the reactions of simple free radicals and chemically reactive intermediates. This mechanism explains the large yield of ammonium chloride and the unusually high abundance of cyano groupings, but unfortunately has the same shortcomings that are inherent in most studies of this kind in that many if not all of the intermediates suggested are inferred from stable product yields. It should also be noted that the explanation for the exceptionally high G value for carbon-chlorine bond rupture of 10.5 is not obvious from the work completed up to this point. Values of G(C-Cl) in related systems were observed to be in the range of 4 to 5.

Because of these uncertainties in the initially proposed radiolysis mechanism, a second phase of research on the carbon tetrachloride-ammonia system was initiated. The purpose of these investigations was to obtain more information about chemically reactive intermediates and about primary and secondary radiolytic processes.

Reactions of Cyanogen Bromide and Ammonia

Introduction

Several methods are commonly used by chemists to establish the presence of an intermediate in organic and inorganic reaction mechanisms. One approach involves the actual isolation and analysis of the chemical transient. This method undoubtedly provides the best evidence for the existence of the intermediate but in most cases is found impractical due to the reactivity of these species. A second method, which can be described as a physical approach to the problem, is based on the measurement of some physical property of the intermediate. Optical spectroscopy, electron spin resonance spectroscopy, and mass spectrometry have been invaluable in this regard. Another way of detecting intermediates is by trapping experiments. This method involves adding a substance to the reaction mixture which does not react with either starting material or the product but will react with transients.

In the present investigation of the gamma ray decomposition of carbon tetrachloride and ammonia solutions, the intermediate for which evidence was being sought was cyanogen chloride. Initially, an attempt was made to isolate this species, but this proved unfruitful, Infrared and ultraviolet analysis of the irradiated solution also met with little success.

It was decided that a valid approach to confirming the role of cyanogen chloride as a reaction intermediate would be to investigate the nature of the products obtained from the direct reaction of this compound with ammonia. At the time this work was undertaken, cyanogen chloride could not be obtained commercially, but cyanogen bromide was available. Accordingly, pure cyanogen bromide was reacted with ammonia in carbon tetrachloride solvent and the resulting products were compared with those from the radiolysis experiments. The similarity between the product distributions from these two different investigations was then taken as a measure of the importance of cyanogen chloride in the radiolytic work.

Results and Discussion

In the first experiment with cyanogen bromide and ammonia, ammonia gas was bubbled into a reaction vessel containing 2.75 g. of cyanogen bromide and 150 ml. of carbon tetrachloride. During the experiment, the reaction mixture was constantly stirred and the temperature kept at 25 ± 2°C. After 1.5 hours the reaction was terminated, and the solid phase products were removed by filtration; 3.2 g. of white crystalline material was recovered. Product analyses showed the mixture to consist of 55.5 mole % ammonium bromide, 41.0% ammonium dicyanamide, 2.3% guanidine hydrobromide, and 1.3% cyanoguanidine. The products identified accounted for 99% (by weight) of the total product yield.

In a subsequent experiment, a solution made up of 2.60 g. of cyanogen bromide in 50 ml. of carbon tetrachloride was added dropwise to 100 ml. of ammonia-saturated carbon tetrachloride. (The solution was resaturated approximately every ten minutes.) The latter experiment is more analogous to the radiolytic work and as expected gave somewhat similar product yields. The product distribution from this reaction was 65.7 mole % ammonium bromide, 27.5% ammonium dicyanamide, 4.7% guanidine hydrobromide, and 2.1% cyanoguanidine. No cyanamide was detected in this mixture. However, virtually any reasonable reaction scheme leading from cyanogen bromide to the observed products would have to involve this intermediate.

The five minor unidentified products appearing in the radiolysis experiments (e.g. the TLC bands A, B, C, C, and E) were not observed in the cyanogen bromide and ammonia reactions. These results strongly suggest that compounds A, B, C, D, and E are probably formed by reactions of N_2H_3 and CCl_3 radicals.

Products from the Photolysis of Carbon Tetrachloride-Ammonia Solutions at 2537 Å

Introduction

In the cyanogen bromide-ammonia experiments chemical evidence was obtained which indicates that cyanogen chloride and very probably cyanamide are important intermediates in the radiolysis of carbon tetrachloride and ammonia. Still unanswered, however, is the question of what the ultimate precursors of cyanogen chloride are. In the simple radiolysis of carbon tetrachloride, for example, any one of the following fragments might be the source of this intermediate: CCl_3^+, CCl_2^+, CCl^+, CCl_3, CCl_2, and CCl. The purpose of the photolysis study was to selectively produce only one of these fragments, $CCl_3\cdot$, and then to examine the reactions of this species in some detail.

Results and Discussion

In the Hg-2537 photolysis of carbon tetrachloride only one primary photolytic process has been shown to occur[16-19]

$$CCl_4 + hr(2537\text{Å}) \rightarrow \cdot CCl_3 + \cdot Cl \qquad (1)$$

In the case of pure, air-free, dry carbon tetrachloride, this process leads to the formation of two products, hexachloroethane and chlorine. With ammonia* added to the system, the secondary reactions (2) through (5) could also be expected to occur.

$$CCl_3\cdot + NH_3 \rightarrow HCCl_3 + NH_2\cdot \qquad (2)$$

$$Cl\cdot + NH_3 \rightarrow HCl + NH_2\cdot \qquad (3)$$

$$NH_3 \rightarrow NH_4Cl$$

$$NH_2\cdot + NH_2\cdot \rightarrow N_2H_4 \qquad (4)$$

$$\cdot CCl_3 + NH_2 \rightarrow CCl_3NH_2 \qquad (5)$$

Thus, one might predict major photolysis products to be chloroform, ammonium chloride, hydrazine, trichloromethylamine, and hexachloroethane.

In this investigation several 10 ml. samples of air-free, dry carbon tetrachloride-ammonia solution were photolyzed for 3 hours using a Hg-2537 light source (average intensity 1.6 x 10^{16} quanta/sec.). The resulting products were analyzed for by gas and thin layer chromatography. These experiments showed major photolysis products to be ammonium dicyanamide, ammonium chloride and hexachloroethane. Lesser amounts of the products guanidine hydrochloride and cyanoguanidine were also detected. The three minor compounds in bands A, B, and D, also present in the radiolysis mixture, were not identified (see Figure 32). Nitrogen was not analyzed for in the gas phase but was probably present as a minor product.

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*Ammonia does not absorb at 2537 Å.

From these experimental results the following conclusions have been drawn: (1) In the gamma-radiolysis of solutions of carbon tetrachloride and ammonia, the primary fragment, CCl_3, is an important source of cyanogen chloride; (2) the formation of the latter intermediate is the result of the sequential decomposition of trichloromethylamine (formed in reaction 5) and dichloromethyleneimine as suggested in the earlier radiolysis mechanism; and (3) hydrazine, in both the photolysis and radiolysis systems, is apparently consumed by NH_2 radicals or other reactive fragments.

It should also be noted that, on the basis of the chloroform yields in related systems, the activation energy for reaction (2) must be taken as greater than 10 kcal. per mole.

The Microwave Glow Discharge of Mixtures of Carbon Tetrachloride and Ammonia

Introduction

From the cyanogen bromide and UV photolysis investigations, chemical evidence was obtained which indicates that the species

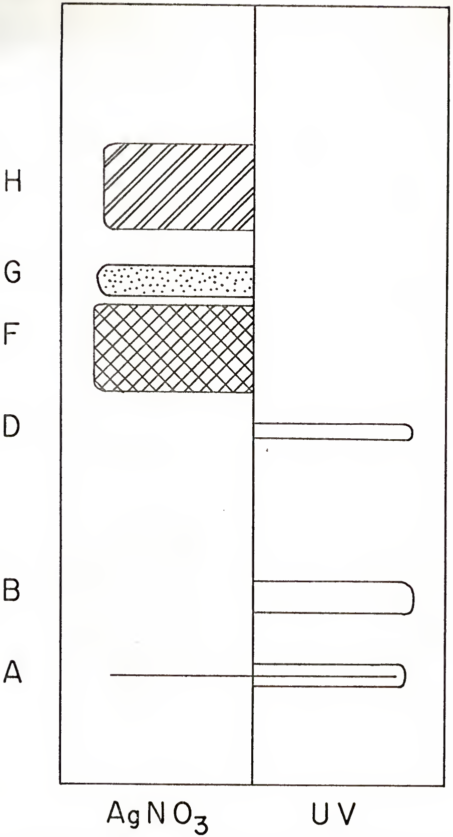

Figure 32. Sketch of a developed cellulose TLC plate showing the separation of 10 mg. of solid phase photolysis products.

trichloromethylamine, dichloromethyleneimine, cyanogen chloride, and cyanamide are important intermediates in the radiolysis mechanism. In the microwave glow discharge experiments described below an attempt is made to observe these species directly using fast flow techniques.

Results and Discussion

In the current investigation two types of experiments were carried out. The first experiment involved discharges in mixtures of carbon tetrachloride and ammonia; the second was a so-called downstream experiment where only one reactant was passed through the discharge zone and the second reactant was bled in downstream. The direct observation of the transients formed in these experiments was achieved by coupling the fast flow reaction tube to a Time-of-Flight mass spectrometer. Details of the apparatus and experimental techniques can be found in Section II.

The results of the mixture experiments can be seen in Figure 33. This figure shows the variation in the relative parent ion intensities of several stable products with changes in per cent composition of the mixture. Stable products are defined here as those chemical species which do not undergo further chemical reactions during the maximum residence time in the present experiments, which was 60 to 70 milliseconds. The products cyanogen chloride and trichloromethylamine are shown here reaching their maximum yields at a composition 60% in carbon tetrachloride. It is reasonable to expect that in an approximately equimolar mixture the ratio of $CCl_3\cdot$ to $NH_2\cdot$ radical concentrations should approach unity, and hence, the yield of CCl_3NH_2 should maximize.

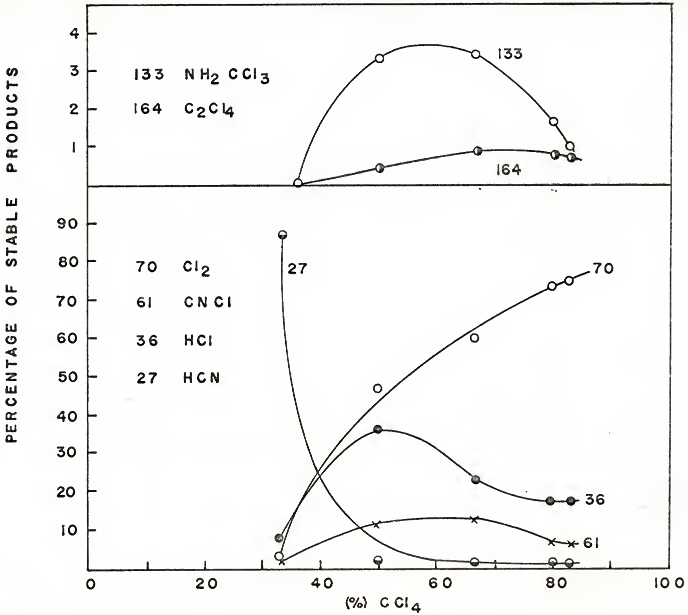

Figure 33. Variation in product distribution with composition in microwave discharge experiments.

To demonstrate that trichloromethylamine was not primarily a product of ion-molecule reactions, a comparison was made of product yields from experiments with pure carbon tetrachloride and those with carbon tetrachloride-ammonia mixtures. In the first case hexachloroethane was the principle high molecular weight product detected. With added ammonia the peaks of hexachloroethane decreased to nearly zero and a corresponding increase appeared for the peaks of trichloromethylamine. Since, in some related experiments it was shown that ion-molecule reactions do not occur in pure carbon tetrachloride up to 60 microns pressure, it must follow that the observed changes in the hexachloroethane and trichloromethylamine yields with added ammonia simply reflect the competitive reactions of CCl_3 radicals, e.g.

$$\cdot CCl_3 + \cdot CCl_3 \rightarrow C_2Cl_6$$

and, $$\cdot CCl_3 + \cdot NH_2 \rightarrow CCl_3NH_2$$

An apparent anomaly in the results shown in Figure 33 is the complete lack of the product dichloromethyleneimine, Cl_2CNH. This is surprising because results of the photolysis study indicated that cyanogen chloride is formed from the sequential decomposition of tricloromethylamine and dichloromethyleneimine.

To determine whether the trichloromethylamine was undergoing rapid conversion to cyanogen chloride, the distance between the discharge zone and the detector was approximately doubled. Results from this experiment showed that with an increase in residence time of 30 milliseconds the ion intensities of cyanogen chloride and trichloromethylamine were unchanged. It was concluded, therefore, that the cyanogen chloride was not formed through the intermediates trichloromethylamine or dichloromethyleneimine.

To obtain further information about the origin of cyanogen chloride, two downstream experiments were carried out. In the first experiment the discharge fragments from carbon tetrachloride were streamed into ammonia; in the second, the discharge fragments of ammonia were streamed into carbon tetrachloride. These experiments clearly showed that only in the former experiment was cyanogen chloride formed.

Of the possible neutral carbon tetrachloride fragments which might react with ammonia to yield cyanogen chloride (e.g. CCl_3, CCl_2 and CCl), CCl_3 radicals were immediately ruled out on energetic grounds. The two remaining fragments CCl_2 and CCl could react with ammonia as follows:

$$CCl_2 + NH_3 \rightarrow ClCN + H_2 \qquad \Delta H = -68 \qquad (1)$$

$$CCl + NH_3 \rightarrow ClCN + H_2 + H \qquad \Delta H = -35 \qquad (2).$$

Although the thermodynamics of these two reactions seem to favor process (1), other evidence available would indicate the second as the more probable. Safrany, Reeves, and Harteck,[20] for instance, have shown that when CH radicals are generated in hydrocarbon flames, addition of ammonia to the system leads to the formation of hydrogen cyanide, e.g.

$$CH + NH_3 \rightarrow HCN + H_2 + H$$

Also of considerable importance is the work of Venkateswarlu.[21] He examined the UV absorption spectrum of fragments produced from electrical discharges in carbon tetrachloride. His results showed that CCl radicals are the principal species present.

The lifetime of the reacting CCl or CCl_2 species was obtained by performing a series of experiments in which the distance between the discharge zone and the ammonia inlet was varied. The results are shown in Figure 34. Using a measured flow-rate of 10 to 15 m./sec., an approximate lifetime of 25 to 30 milliseconds was found.

An Electron Impact Study on Mixtures of Carbon Tetrachloride and Ammonia in a High Pressure Ion Source

Introduction

Over the last fifteen years radiation chemists and mass spectroscopists have had frequent occasion to study the reactions of ions in the gas phase. Among the different types of ion reactions which have been investigated are the following:

$$(A^+)^* \rightarrow M^+ + N \qquad (1)$$

(dissociation of an excited molecular ion into a second molecular ion and a molecule)

$$(A^+)^* \rightarrow R^+ + S\cdot \qquad (2)$$

(dissociation of an excited molecular ion into a carbonium ion and a radical)

$$A^+ + B \rightarrow A + B^+ \qquad (3)$$

(charge transfer)

$$A^+ + B \rightarrow C^+ + D \qquad (4)$$

(ion-molecule reaction)

$$A + e^- \rightarrow A^- \qquad (5)$$

(electron capture)

$$A + e^- \rightarrow B^- + C \qquad (6)$$

(dissociative electron capture)

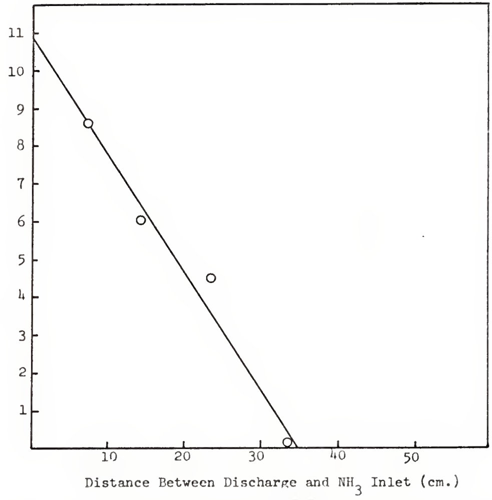

Figure 34. Formation of cyanogen chloride by addition of ammonia downstream from the glow discharge of carbon tetrachloride.

In this investigation attention will be focused primarily on ion-molecule reactions. Gas phase studies have shown that when reactions of this type are exothermic no activation energy is required and the reaction takes place at the first collision. Several examples of ion-molecule reactions which are relevant to gas phase radiation chemistry are given below:

Methane System[22,23] $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

$CH_4^+ + CH_4 \rightarrow CH_5^+ + \cdot CH_3$

Ammonia System[24,25] $NH_3^+ + NH_3 \rightarrow NH_4^+ + \cdot NH_2$

$NH_2^+ + NH_3 \rightarrow N_2H_4^+ + \cdot H$

Rate constants for these reactions are all larger than 1×10^{-10} cc/molecule/sec.

Very little information is available on ion-molecule reactions in the liquid phase. In one study carried out by Lampe, Field, and Franklin[26] it was shown that in the radiolysis of water the initially formed H_2O^+ ion reacts very rapidly with water molecules to form H_3O^+ and a hydroxyl radical, i.e.

$$H_2O^+ + H_2O \rightarrow H_3O^+ + \cdot OH \qquad (1)$$

The authors give the lifetime of H_2O^+ in liquid water as about 1.6×10^{-14} sec. Their results indicate that the above reaction precedes the neutralization process represented as

$$H_2O^+ + e^- \rightarrow (H_2O)^* \rightarrow H\cdot + OH\cdot \qquad (2)$$

More recently, Busler, Martin, and Williams [27] studied the radiolysis of dilute solutions of deuterated ammonia in cyclohexane (.1 to .02 M ND_3). These authors observed the formation of HD in yields in excess of the "statistical expectation." They explained their results in terms of proton transfer reactions, e.g.

$$c\text{-}C_6H_{12}^{+} + ND_3 \rightarrow c\text{-}C_6H_{11}\cdot + ND_3H^{+} \qquad (1)$$

followed by

$$ND_3H^{+} + e^{-} \begin{array}{l} \nearrow ND_3 + H\cdot \\ \searrow ND_2H + D\cdot \end{array} \qquad (2)$$

and

$$D\cdot + c\text{-}C_6H_{12} \rightarrow HD + c\text{-}C_6H_{11}\cdot \qquad (3)$$

These experiments indicated that ion lifetimes in irradiated cyclohexane were in the range of 10^{-8} to 10^{-9} sec.

In the present study on the gamma radiolysis of dilute solutions of carbon tetrachloride and ammonia, there are three ionic fragments that could be formed which might react with the solute ammonia via ion-molecule reactions (e.g. CCl_3^{+}, CCl_2^{+}, and CCl^{+}). These fragments would presumably be the products of the primary processes shown below in reactions (1), (2), and (3).

$$CCl_4 + \underline{e}^{-} \rightarrow CCl_3^{+} + Cl^{-} + \underline{e}^{-} \qquad (1)$$

$$CCl_4 + \underline{e}^{-} \rightarrow CCl_2^{+} + Cl_2 + e^{-} + \underline{e}^{-} \qquad (2)$$

$$CCl_4 + e^{-} \rightarrow CCl^{+} + Cl_2 + Cl^{-} + \underline{e}^{-} \qquad (3)$$

Of the three processes listed, available mass-spectrometric data[28] indicates that reaction (1) is probably the most important (see Table V). In solutions containing ammonia, the CCl_3^{+} ions could be expected to react in one of two ways:

$$CCl_3^{+} + Cl^{-} \rightarrow (CCl_4)^{*} \rightarrow CCl\cdot_3 + Cl\cdot \qquad (4)$$

or

$$CCl_3^{+} + NH_3 \rightarrow (CCl_3NH_3^{+})^{*} \qquad (5)$$

The first reaction shows the neutralization of CCl_3^{+} by Cl^{-} with the resulting formation of the probable species $\cdot CCl_3$ and $\cdot Cl$. Reaction (5)

TABLE V

FRAGMENTATION PATTERN OF CARBON TETRACHLORIDE AT 70 E.V.*

Ion	Intensity	A.P.
CCl_4^+	.02	11.0
CCl_3^+	100.	12.2
CCl_2^+	23.5	16
CCl^+	27.8	17
Cl_2^+	.35	16
Cl^+	27.6	19
C^+	14	23
CCl_3^{++}	1.6	31.8
CCl_2^{++}	.8	34
Cl^-	99.5	1.3 5.8 12.4
Cl_2^-	.1	4.8
C^-	.01	-
CCl^-	.005	-

*R. F. Baker and J. T. Tate, Phys. Rev., 53, 683 (1938) is an ion-molecule reaction yielding the excited complex $CCl_3NH_3^+$. It is common to refer to this type of process as a sticky collision. It is also to be noted that reaction (5) can be thought of as a Lewis acid-base reaction. Here, the carbonium ion CCl_3^+ is the Lewis acid, and ammonia with its unshared electron pair is the Lewis base.

To establish the possible importance of the $CCl_3NH_3^+$ ion in the radiolysis work, a series of experiments were carried out in a high pressure ion source of a Bendix Time-of-Flight Mass Spectrometer. In these experiments ion-molecule reactions were studied over the pressure range 3.5 to 80 μ using a gas mixture consisting of 50% carbon tetrachloride and 50% ammonia.

Results and Discussion

The results of the above experiments can be seen in Figures 35 and 36. These figures show the change in the relative ion intensity of the species $CCl_3NH_3^+$, $CCl_2NH_2^+$, CCl_3^+, CCl_2^+, NH_3^+, and NH_4^+ as a function of the absolute pressure. The relative yields given represent the fraction of the total observed ion intensity which is due to the species in question. An analysis of the ion curves in these figures reveals the following trends: At low pressures (3.5 μ), the principal mixed secondary ion is $CCl_2NH_2^+$. The intensity of this ion reaches a maximum at approximately 7 μ. Also at this pressure a second mixed ion appears, $CCl_3NH_3^+$. As the $CCl_2NH_2^+$ ion decays, the $CCl_3NH_3^+$ ion continues to increase until a pressure of 30 μ is reached. Beyond 30 μ pressure, the $CCl_3NH_3^+$ ion intensity also decreases sharply. The primary ion CCl_3^+ increases in intensity over the pressure range 3.5 to 18 μ but then decreases again at still higher pressures. At 81 μ the ion intensity of

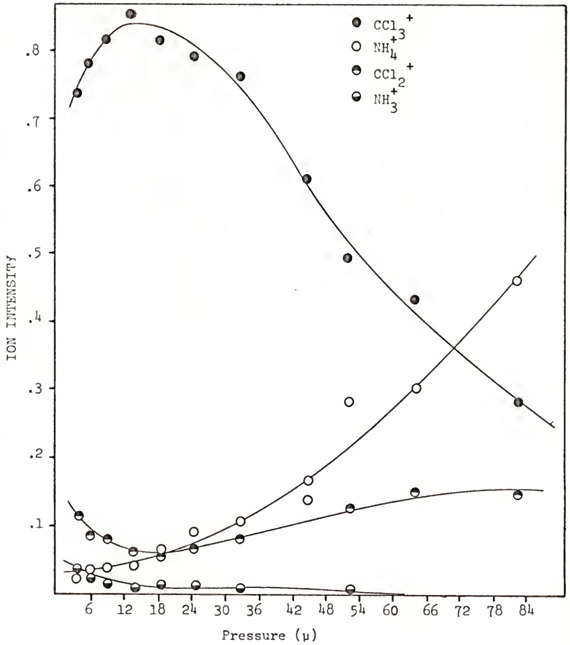

Figure 35. Variation of the relative ion intensities of CCl_3^+, CCl_2^+, NH_3^+, and NH_4^+ with pressure.

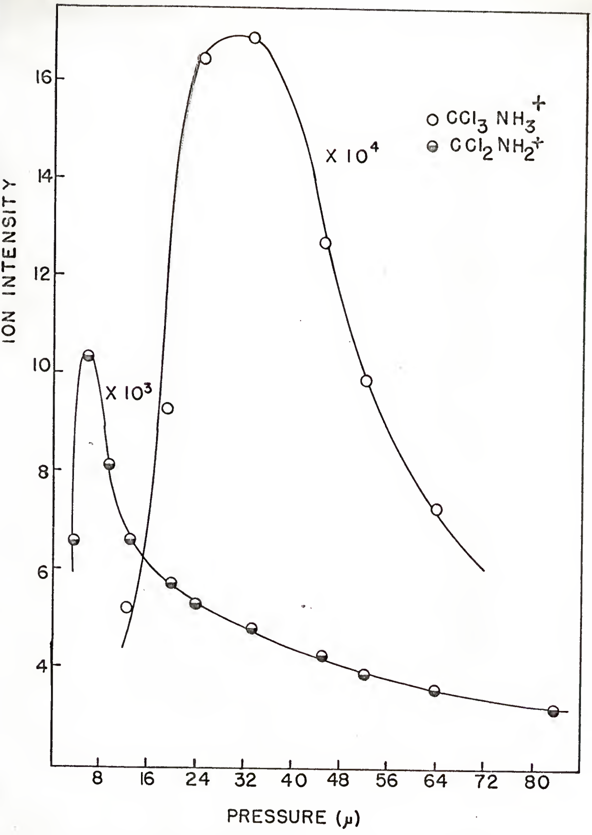

Figure 36. Variation of the relative ion intensities of $CCl_3NH_3^+$ and $CCl_2NH_2^+$ with pressure.

CCl_3^+ was 30% of that at 18 μ. The only other ion displaying a sizable change in intensity was NH_4^+. It increases steadily over the pressure range 3.5 to 81 μ, surpassing the intensity of the primary ion CCl_3^+ at approximately 70 μ.

To explain the above changes in ion intensity with pressure for the ions CCl_3^+, NH_4^+, $CCl_3NH_3^+$, and $CCl_2NH_2^+$, the following mechanism is proposed:

	$CCl_3^+ + NH_3 \rightarrow (CCl_3NH_3^+)*$	(1)[≠]
Low Pressures	$(CCl_3NH_3^+)* \rightarrow CCl_2NH_2^+ + HCl$	(2)
Medium Pressures	$(CCl_3NH_3^+)* + M \rightarrow CCl_3NH_3^+$	(3)
High Pressures	$(CCl_3NH_3^+)* + M \rightarrow CCl_3NH_3^+$	(4a)
	$CCl_3NH_3^+ + NH_3 \rightarrow CCl_3NH_2 + NH_4^+$	(4b)

This mechanism suggests that CCl_3^+ ions first react with ammonia molecules to form an excited complex of $CCl_3NH_3^+$. Subsequent reactions are then determined by the pressure of the gas mixture. At low pressures, for example, $(CCl_3NH_3^+)$ readily decomposes to yield $CCl_3NH_2^+$ and an HCl molecule. At higher pressures (10 μ), $(CCl_3NH_3^+)^*$ is collisionally deactivated; hence, the increase in the $CCl_3NH_3^+$ peak and the decrease in $CCl_2NH_2^+$. At very high pressures (32 μ) $CCl_3NH_3^+$, being a weaker base than ammonia, undergoes a proton transfer reaction with another ammonia molecule to give CCl_3NH_2 and NH_4^+. This would explain the sharp increase in the intensity of the NH_4^+ ion and the corresponding decrease in CCl_3^+. That the observed increase in the NH_4^+ ion intensity is not the result of an ion-molecule reaction involving NH_3^+, e.g.

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + \cdot NH_2$$

[≠] An asterisk in these equations and in the subsequent paragraph indicates that the species in question is in an excited state.

can be seen from Figure 35. Here, the total change in NH_3^+ over a pressure range of 80 μ is .03 relative ion intensity units; the increase in NH_4^+ is .5.

Although the importance of the CCl_2^+ and CCl^+ ions has not been stressed, the data collected in these experiments seem to indicate that reactions between these ions and ammonia might be the source of the minor secondary ions $ClCN^+$, $ClCNH^+$, and $ClCNH_2^+$.

The explanation for the increase in the CCl_3^+ ion intensity with increasing pressure up to 18 μ is not particularly clear. This phenomenon was also observed in some studies on pure carbon tetrachloride.

To provide additonal evidence for the proposed ion-molecule reaction mechanism, an attempt was made to measure appearance potentials for several of these processes. Unfortunately, these experiments met with little success, and no further evidence can be offered at this time.

Tetrachloroethylene Scavenger Studies

Introduction

In radiolysis studies on liquid phase systems, it is common to divide the total observed product yield into two categories designated as the radical and molecular yields. The distinction between these yields is based on the effect on the system of free radical scavengers such as I_2, Br_2, HI, O_2, NO, DPPH, olefins, etc. These reagents have low activation energies (e.g. 0 to 3 kcal.) for reaction with free radicals and thus prevent the formation of radiolysis products resulting from steady-state radical recombination. The portion of the yield so affected is called the free radical yield. There are several other processes leading to radiolysis products which are not affected by scavengers at millimolar concentrations. These include hot atom reactions, true molecular eliminations, ion-molecule reactions, and radical-radical recombination in tracks and spurs.* Collectively, these processes are responsible for the molecular yield.

When the radical scavenger concentration exceeds .01M, radical-radical recombination in the spurs is also affected. In systems containing high concentrations of scavengers, therefore, only those products formed from unimolecular elmination processes and hot atom and ion-molecule reactions are found to be important.

Earlier, in the high pressure electron impact investigation, it was shown that over a pressure range of 3.5 to 80 μ ion-molecule reactions do occur between CCl_3^+ ions and ammonia. In the radiolytic experiments described below, evidence was being sought which would indicate that ion-molecule reactions are also important in the liquid phase. In these experiments carbon tetrachloride solutions containing two mole per cent ammonia and eight mole per cent of the free radical scavenger tetrachloroethylene were irradiated. Under these conditions, it is to be expected that all products originating from steady-state radical reactions (e.g. those reactions involving freely diffusing chlorine atoms and NH_2 and CCl_3 radicals) would be completely inhibited. Products produced from spur reactions, however, should be only partially affected.

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*In liquids or solids, ionizing radiations deposit a considerable amount of their energy in small regions called spurs. These spurs are approximately 10-20Å in diameter, contain typically two or three primary ionizations and involve deposition of about 50 to 100 e.v. In the case of densely ionizing radiations such as particles, the spurs overlap into a continuous track.[29]

In the present experiments, since products arising from both hot atom reactions and unimolecular elimination processes are probably unimportant, the formation of the organic nitrogen compounds ammonium dicyanamide, cyanoguandine, and guanidine hydrochloride can be taken as a measure of the probable importance of ion-molecule reactions in the system carbon tetrachloride-ammonia.

The selection tetrachloroethylene over other possible radical scavengers in these experiments was made for the following reasons: (1) addition of this scavenger minimized the number of new products formed in the system; (2) tetrachloroethylene is at least somewhat similar to the principal starting material, carbon tetrachloride; and (3) no charge transfer should occur between CCl_3^+ and tetrachloroethylene.

Results and Discussion

To a 4 ml. sample of carbon tetrachloride containing 2 mole % ammonia, 3.6×10^{-3} moles of tetrachloroethylene was added. This sample was irradiated for 5.5 hours at a dose rate of $.590 \times 10^{18}$ e.v./ml./min. The solid phase product yield from this experiment was 20 mg. Analysis of the sample by thin layer chromatography revealed bands corresponding to A, B, D, F, G, and H on earlier TLC plates. Ultraviolet spectra of the extracted compounds verified that all formerly identified radiolysis products were present in the above sample mixture.* Although no quantitative analyses were carried out, a comparison between several TLC plates indicated roughly the same product distribution for experiments both with and without scavenger.

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*In this experiment, it is reasonable to assume that a certain fraction of the product mixture consisted of polymeric material.

Further evidence supporting the importance of ion-molecule reactions in the radiolysis work was provided by some Hg-2537 photolysis experiments. Under these conditions only $\cdot CCl_3$ radicals, chlorine atoms, and possibly $\cdot NH_2$ radicals would be generated. With added tetrachloroethylene, therefore, no solid phase products should be produced. The results of these experiments showed that after one hour of photolysis only trace amounts of solid phase materail were observable. Justification for using tetrachloroethylene as a radical scavenger in these experiments was found in the work of Hummel, Lacher, Bohmfalk, and Park.[30] These authors showed that although tetrachloroethylene has an extinction coefficient of .3 atm.$^{-1}$ cm.$^{-1}$ at 2537 Å, absorption at this wavelength does not lead to bond rupture. Thus, in the present system electonically excited tetrachloroethylene would be expected to undergo either energy transfer to carbon tetrachloride or be collisionally deactivated.

From the results of the electron impact and tetrachloroethylene scavenger investigations, the following interpretation of ionic processes in the gamma-radiolysis of carbon tetrachloride-ammonia solutions is suggested.

In the gamma radiolysis of pure carbon tetrachloride two primary ionic processes are important:

$$CCl_4 + \underline{e}^- \rightarrow CCl_3^+ + Cl\cdot + e^- + \underline{e}^- \qquad (1)$$

and,

$$CCl_4 + \underline{e}^- \rightarrow CCl_3^+ + Cl^- + \underline{e}^- \qquad (2).$$

The appearance potentials for these processes are between 11 and 13 e.v. However, since the average energy to form an ion pair during gamma radiolysis of a liquid is of the order of 30 e.v.,[31] the fragments and electrons formed in these reactions may be born with considerable excess kinetic energy and immediately begin to diffuse apart. Because of mass considerations, chlorine atoms, chloride ions and electrons are expected to be the major diffusing species. Considering for the moment the diffusing electron from reaction (1), the Samuel and Magee model[32] predicts that this electron would travel a distance of about 20 Å (approximately 4 carbon tetrachloride molecular diameters) from the primary fragment CCl_3^+ before being reduced to thermal energy. At this distance the electron is still within the electrostatic field of the CCl_3^+ ion, but in carbon tetrachloride it is not necessarily drawn back to the positive ion to cause its neutralization. Instead, it may be removed in a dissociative electron capture process, e.g.

$$CCl_4 + e^- \rightarrow \cdot CCl_3 + Cl^- \qquad (3)$$

(The resonance energies for this reaction are 1.3 ± .5 e.v., 5.8 ± .5 e.v. and 12.5 ± .2 e.v.)[33] The principal neutralization process in the system is probably the reaction

$$Cl^- + CCl_3^+ \rightarrow (CCl_4)^* \rightarrow CCl_3\cdot + Cl\cdot \qquad (4)^{\ddagger}$$

This will also be true for the primary process represented by reaction (2). In that case, however, the Cl^- ion will probably be thermalized within one or two molecular diameters of the positive ion. With 2 mole % ammonia added to the system, each CCl_3^+ ion has, on the average, one ammonia molecule two molecular diameters away from it and 4 or 5 molecules at three molecular diameters. Under these conditions, the CCl_3^+ can react not only via process (4) but also by the reaction shown below.

[‡] According to J. L. Magee[34] it is probable that the intermediate excited molecule is not actually formed, because electron transfer occurs at a distance considerably greater than the ordinary bond distance.

$$CCl_3^+ + NH_3 \rightarrow (CCl_3NH_3^+)^* \qquad (5)$$

Aside from the experimental evidence, this conclusion is based on the fact that the estimated time for neutralization in the condensed phase (e.g. reaction (4)) is 10^{-13} to 10^{-12} sec.; whereas, ion-molecule reactions (again in the condensed phase) are believed to take place in a time of the order of 10^{-14} to 10^{-13} sec.[35] Because of the close proximity of the Cl^- ion to CCl_3^+ in the primary process shown in reaction (2), it is probable that only CCl_3^+ fragments formed in reaction (1) participate in reaction (5).

It was noted earlier that the G value for carbon-chlorine bond rupture in the present system (e.g. 10.5) is considerably higher than the value predicted on the basis of some related radiolysis studies (e.g. 4 or 5).[1,3,4,5] To explain this unusually high value of G(C-Cl), two possibilities were considered: (1) "track effects"; and (2) the influence of ion-molecule reactions. The first possibility was ruled out on the grounds that in the studies currently being compared there were no major differences in either radiation types or radiation dose rates (the two factors leading to "track effects"). The second possibility, that is, that ionic processes are responsible for the increased value of G(C-Cl), is based on the well established fact that radical species formed from the dissociation of an excited species in the liquid phase do not always succeed in escaping recombination. In some cases the closely packed molecules surrounding the radicals lead to recombination in a time not much greater than 10^{-13} sec. This has been referred to by Franck and Rabinowitch[36] as the "cage effect." More recently, Noyes[37,38] has pointed out that even for those radicals which have diffused two or three molecular diameters away from each other there is still a reasonably high probability that they will recombine with their original partners. He refers to this process as "secondary recombination" in contrast to the process of "primary recombination" described by Franck and Rabinowitch. It is now common to refer to these recombination processes collectively as "geminate recombination." Noyes has estimated that for the dissociation of iodine in hexane the probability of geminate recombination is about 0.5.

In the radiolysis of carbon tetrachloride systems, it is to be expected that if reactions (1), (2), (3), and (4) are the principal reactions leading to the formation of stable products, then the value of G(C-Cl) will depend to a large extent on the efficiency with which radicals formed in reaction (4) escape geminate recombination. In the particular system carbon tetrachloride and ammonia, an alternate reaction scheme has been shown to lead to product formation, namely, reactions (1), (3) and (5). This sequence provides a route in which geminate recombination is effectively bypassed. It is concluded, therefore, that in the present system it is the ionic reaction sequence, (1), (3), and (5), that is responsible for the observed increase in the G value for carbon-chlorine bond rupture.

SECTION IV

SUMMARY AND CONCLUSIONS

Mechanism of the Gamma Radiolysis of Carbon Tetrachloride-Ammonia Solutions

The various investigations described here have led to the following observations and conclusions concerning the gamma radiolysis of carbon tetrachloride-ammonia solutions: (1) the major radiolysis products are ammonium chloride, ammonium dicyanamide, and hexachloroethane; (2) minor products include cyanoguanidine, guanidine hydrochloride, and nitrogen; (3) the absence of hydrazine as a major radiolysis product is due principally to secondary reactions involving $NH_2\cdot$ radicals; (4) the large G value of ammonium chloride does not indicate a chain process but merely reflects the stoichiometry of the reaction; (5) trichloromethylamine, dichloromethyleneimine, cyanogen chloride, and cyanamide are all chemically reactive intermediates which are part of a reaction sequence leading to the formation of the organic nitrogen compounds; (6) both ionic and free radical processes lead to the formation of trichloromethylamine; and (7) the large G value for carbon-chlorine bond rupture is explainable in terms of the ion-molecule reactions of the primary ion CCl_3^+.

These findings are summarized below in reactions 1 through 21. Brackets have been placed around several groups of reactions to indicate their approximate position on a relative time scale of events, those groups at the top taking place in the shortest time and the ones at the bottom taking the longest.

$$CCl_4 + \underline{e}^- \rightarrow CCl_3^+ + Cl\cdot + \underline{e}^- + e^- \tag{1}$$
$$CCl_4 + \underline{e}^- \rightarrow CCl_3^+ + Cl^- + \underline{e}^- \tag{2}$$
$$CCl_4 + e^- \rightarrow \cdot CCl_3 + Cl\cdot + \underline{e}^- \tag{3}$$
$$CCl_4 + e^- \rightarrow \cdot CCl_3 + Cl^- \tag{4}$$

$$CCl_3^+ + NH_3 \rightarrow CCl_3NH_3^+ \tag{5}$$
$$CCl_3^+ + Cl^- \rightarrow \cdot CCl_3 + Cl\cdot \tag{6}$$

$$CCl_3NH_3^+ + NH_3 \rightarrow NH_2CCl_3 + NH_4^+ \tag{7}$$
$$\cdot CCl_3 + \cdot CCl_3 \rightarrow C_2Cl_6 \quad \text{(spurs)} \tag{8}$$
$$\cdot CCl_3 + Cl\cdot \rightarrow CCl_4 \quad \text{(primary recombination)} \tag{9}$$
$$Cl\cdot + NH_3 \rightarrow HCl + NH_2\cdot \tag{10}$$

$$\cdot CCl_3 + \cdot NH_2 \rightarrow CCl_3NH_2 \tag{11}$$
$$\cdot CCl_3 + \cdot CCl_3 \rightarrow C_2Cl_6 \tag{12}$$
$$\cdot NH_2 + \cdot NH_2 \rightarrow N_2H_4 \tag{13}$$
$$\cdot NH_2 + N_2H_4 \rightarrow \cdot N_2H_3 + NH_3 \tag{14}$$
$$\cdot N_2H_3 + \cdot N_2H_3 \rightarrow 2NH_3 + N_2 \tag{15}$$

$$NH_2CCl_3 \rightarrow HN{=}CCl_2 + (HCl) \tag{16}$$
$$HN{=}CCl_2 \rightarrow Cl{-}C{\equiv}N + (HCl) \tag{17}$$
$$Cl{-}C{\equiv}N + NH_3 \rightarrow NH_2C{\equiv}N + (HCl) \tag{18}$$
$$NH_2C{\equiv}N + Cl{-}C{\equiv}N \rightarrow H{-}N(CN)_2 + (HCl) \tag{19}$$
$$\llcorner NH_3 \rightarrow NH_4^+N(CN)_2^-$$
$$NH_2C{\equiv}N + NH_3 \rightarrow (H_2N)_2C{=}NH \tag{20}$$
$$\llcorner (HCl) \rightarrow (H_2N)_2C{=}NH_2^+Cl^-$$
$$NH_2C{\equiv}N + NH_2C{\equiv}N \rightarrow (H_2N)_2C{=}N{-}C{\equiv}N \tag{21}$$

Still unanswered in this work is the possible importance of the species ·CCl and CCl_2 . In the microwave experiments it was shown that one or both react with ammonia to give cyanogen chloride. It is conceivable that they also react in a similar manner in the liquid phase.

Comparison of the Gamma Radiolysis and Thermolysis of Carbon Tetrachloride-Ammonia Solutions

It has been reported by Anderson[39] that under normal laboratory conditions mixtures of carbon tetrachloride and ammonia yield no detectable products. Stahler[40] has reported, however, that at 140°C (i.e. above the critical temperature of ammonia) carbon tetrachloride does react with ammonia in the presence of copper and iodine to provide a 35-40% yield of guanidine together with lesser quantities of hydrocyanic acid or cyanogen. Watt and Hahn,[41] on the other hand, found that carbon tetrachloride and ammonia do not react at any appreciable rate at temperatures below 300°C. In addition, they found that potassium and ammonium iodide were far more effective as catalysts for the ammonolysis reaction than copper and iodine; the former gave yields of guanidine as high as 80%. No additional products, other than ammonium chloride, were reported.

Although there are differences in the method of activation, temperature, phase, and relative concentrations of carbon tetrachloride and ammonia, a comparison of the present work with that of Watt and Hahn seems to indicate that the same basic reaction scheme, reactions (3) through (21), can be applied to the two reaction systems. Watt and Hahn, for example, speculated that cyanogen chloride might also be an important intermediate in the thermally induced reaction. This species could be formed in the same manner as in the radiolysis experiments, from reaction sequences (5), (7), (16), (17), or (11, (16), (17). The reaction could be initiated either by homolytic or heterolytic thermal bond rupture. Since ionic salts acted as excellent catalysts in these experiments, it appears that heterolytic cleavage followed by reactions (5), (7), (16) and (17) constitute the most important reaction sequence for the system studied by Watt and Hahn.

The chief differences between the thermal and radiolytic reactions occurs in the competitive reactions (19), (20), and (21). Only one of these, (20), involves ammonia as a reactant. It would therefore be relatively more rapid in the experiments of Watt and Hahn, owing to the higher concentrations of ammonia, and thus give rise to the observed predominant formation of guanidine. Ammonium dicyanamide and cyanoguanidine which are formed from the other two reactions (19 and 21) were identified as major and minor products under radiolysis but were not found in the thermal reaction. It is possible that the failure of the earlier workers to identify these compounds was due to the lack of a sufficiently sensitive analytical procedure, such as thin layer chromatography, rather than their total absence.

Comparison of the Gamma Radiolysis of Carbon Tetrachloride and Ammonia with other Carbon Tetrachloride Systems

The general findings of those studies reveiwed on the radiolysis of dilute solutions of carbon tetrachloride can be summarized in two statements: (1) The G value for carbon-chlorine bond rupture from primary processes is between 4 and 5. And (2), nearly all major radiolysis products from these systems can be explained in terms of single one step radical-radical combinations or radical abstraction reactions.

In contrast to these findings are the results from the ammonia-carbon tetrachloride system. In this case, the G value for carbon-chlorine bond rupture is 10.5, and all identified radiolysis products, with the exception of hexachloroethane, are formed from secondary reactions of the primary products trichloromethylamine and hydrazine. Most important, however, is the finding that in the carbon tetrachloride-ammonia system both free radical and ionic processes lead to the formation of stable products.

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BIOGRAPHICAL SKETCH

Douglas Dale Davis was born in Madrid, Nebraska, on February 23, 1940. He attended high school in Seattle, Washington. He graduated from Highline High School in 1958. In June, 1962, he received the degree of Bachelor of Science from the University of Washington. In 1962 he enrolled in the Graduate School of the University of Florida. Since then he has served as a nuclear research assistant and a graduate fellow in the Department of Chemistry.

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